DOE Site:	Savannah River Site, SC
EM Project:	Tank 48
ETR Report Date:	August 2006

External Technical Review Summary

United States Department of Energy Office of Environmental Management (DOE-EM)

External Technical Review of Tank 48 at the Savannah River Site (SRS)

Why DOE-EM Did This Review

Tank 48 is a 1.3 million gallon tank with full secondary containment, located and interconnected within the SRS tank system that will play a very important role in removal and processing of high-level waste (HLW) in the years ahead. However, the tank is currently isolated from the system and unavailable for use, because its contents. It contains approximately 250,000 gallons of salt solution containing Cesium-137 and other radioisotopes which are contaminated with significant quantities of tetraphenylborate (TPB), a material which can release benzene vapor to the tank head space in potentially flammable concentrations. Plans for SRS HLW processing require removal and disposition of the contents of Tank 48 and its return to service. *The external review objective was to assess the technical viability of the current Washington Savannah River Company (WSRC) path forward for the removal, treatment and disposition of Tank 48 contents.*

What the ETR Team Recommended

The ETR Team recommends the following to improve the probability of timely success:

- Commit to Steam Reforming as the lead TPB processing approach immediately and carry Wet Air Oxidation (WAO) as a back up, to be developed to a point of assuring viability.
- Embark on a high priority heel management project, including development, testing and planning for tank flushing and the establishment of end point criteria for Tank 48 cleanliness..
- Incorporate process steps to improve schedule success (January 2010). Evaluate pre-concentration (e.g. filtration) to reduce the volume to be treated followed by transferring the bulk of the tank contents to another tank (existing or smaller constructed tank) to allow parallel heel processing and flushing. The team believes that these steps will greatly improve the probability of schedule success.
- Continue the development of steam reforming on the earliest practical schedule.

What the ETR Team Found

The ETR Team's over-arching conclusion was that while TPB processing alternatives are being properly and thoroughly evaluated, the issues necessary to achieve *timely* Tank 48 return-to-service have not been fully addressed. In the Team's view, the critical considerations for selection of a primary treatment technology include the (1) ability to produce a treated material compatible with subsequent vitrification at the Defense Waste Processing Facility (DWPF), (2) ability for the necessary process components to physically fit within the space envelope of the 241-96H facility (to avoid construction of a new radiation compliant building), and (3) process maturity to facilitate expeditious testing, design, construction and operation that is consistent to the extent possible with overall SRS schedule constraints. The two TPB processing methods chosen by WSRC as lead candidates (Steam Reforming and WAO) are technically sound, likely viable methods, and offer the best prospects for success among the approximately 80 alternatives considered. However, several areas were identified where the previous evaluations have not been sufficiently complete. Removal of residual material, tank cleanup after removal of the bulk of the material, and understanding of the form, quantities, concentrations and implications of TPB processing by-products are topics which will be very important to success.

To view the full ETR reports, please visit this web site:
http://www.em.doe.gov/Pages/ExternalTechReviews.aspx

July 2009

The purpose of an External Technical Review (ETR) is to reduce technical risk and uncertainty. ETRs provide pertinent information for DOE-EM to assess technical risk associated with projects and develop strategies for reducing the technical risk and to provide technical information needed to support critical project decisions. Technical risk reduction increases the probability of successful implementation of technical scope. In general, ETRs assesses technical bases, technology development, and technical risk identification and handling strategies.

ITR-T48-2006-001
Revision 0

INDEPENDENT TECHNICAL REVIEW (ITR)

of the
PATH FORWARD

for
SAVANNAH RIVER SITE (SRS) TANK 48

August 10, 2006

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REVISION SUMMARY

REVISION	SUMMARY OF CHANGES	AFFECTED PAGES	DATE
0	Initial Issue	N/A	8/10/2006

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ACRONYMS

ARP	Actinide Removal Project
atm	Atmosphere
Cs-137	Cesium 137
CsTPB	Cesium Tetraphenylborate
DDA	Deliquification, Dissolution, and Adjustment
DNFSB	Defense Nuclear Facility Safety Board
DOE	Department of Energy
DOE-SR	Department of Energy–Savannah River
DPP	Disposition Processing Plan
DWPF	Defense Waste Processing Facility
EPA	U. S. Environmental Protection Agency
FFA	Federal Facility Agreement
HLW	High Level Waste
HTF	H-Tank Farm
INL	Idaho National Laboratory
IPM	Initial Processing Module
ITP	In-Tank Precipitation
ITR	Independent Technical Review
IW	Inhibited Water
KTPB	Potassium Tetraphenylborate
LAW	Low-Activity Waste
LOI	Lines of Inquiry
MCU	Modular Caustic Side Solvent Extraction Unit
MST	Monosodium Titanate
NaTPB	Sodium Tetraphenylborate
ORNL	Oak Ridge National Laboratory
SBW	Sodium Bearing Waste
SCDHEC	South Carolina Department of Health and Environmental Control
SPF	Saltstone Production Facility
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
STAR	Science and Technology Applications Research

SWPF	Salt Waste Processing Facility
TCLP	Toxicity Characteristic Leaching Procedure
THOR	THOR Treatment Technologies, LLC
TOC	Total Organic Carbon
TPB	Tetraphenylborate
WAC	Waste Acceptance Criteria
WAO	Wet-Air Oxidation
WGI	Washington Group International
WIPP	Waste Isolation Pilot Plant
WSRC	Washington Savannah River Company

Executive Summary

On June 6th 2006, an Independent Technical Review (ITR) Team convened at the Savannah River Site (SRS) to assess the technical viability of the current Washington Savannah River Company (WSRC) path forward for resolution of the long-standing problems posed by the tetraphenylborate (TPB) contamination in SRS high level waste (HLW) Tank 48[1]. Over the subsequent ten weeks, team members reviewed extensive documentation of previous WSRC work on this issue, were briefed by or interviewed WSRC personnel, toured the tank site, conducted literature searches for information pertinent to this problem, visited facilities where equipment comparable to that anticipated for use at SRS was being operated or tested, and participated in numerous inter-team discussions on this topic.

In the course of its work, the ITR Team conducted detailed reviews of the methods and processes (including backups) comprising the current WSRC path forward for Tank 48, along with several alternative approaches. The Team identified technical and programmatic risks attendant to each, and on that basis formulated a recommended course of action.

This Executive Summary is a synopsis of the ITR, including the ITR Team's key conclusions and recommendations for Tank 48 actions. The ITR full report [ITR-T48-2006-001], with its appendices, provides supporting detail.

Background

Safe management, retrieval, processing and ultimate disposition of the ~36 million gallons of HLW at SRS is a matter of very high priority to the local community, to the State of South Carolina and to the U.S. Government. The U.S. Department of Energy (DOE), the South Carolina Department of Health and Environmental Control (SCDHEC), and U. S. Environmental Protection Agency (EPA) are signatory to a Federal Facility Agreement (FFA) which commits to an aggressive schedule for emptying and permanent closure of non-compliant SRS HLW tanks by 2122.

Tank 48 is a 1.3 million gallon tank, one of the "new style" tanks with full secondary containment, located and interconnected within the SRS tank system that will play a very important role in removal and processing of HLW in the years ahead. However, the tank is currently isolated from the system and unavailable for use, because its contents - approximately 250,000 gallons of salt solution containing Cesium-137 (Cs-137) and other radioisotopes - are contaminated with significant quantities of TPB, a material which can release benzene vapor to the tank head space in potentially flammable concentrations.

[1] The tank's full designation is 241-948H, indicating its presence in the H Area Tank Farm. For simplicity it is referred to throughout this report as "Tank 48".

Tank 48 has been in that condition since 1983, when TPB was first added during a full-scale demonstration of the In-Tank Precipitation (ITP) process. While there have been numerous studies and plans for removal of the tank contents, none has been implemented to date.

Plans for SRS HLW processing, as needed to meet FFA commitments, rely on return-to-service of Tank 48 by January 2010, an aggressive schedule that places very high importance on successful resolution of the TPB problem. Early this year, WSRC established a Tank 48 path forward comprising development and application of one of two processes, Steam Reforming and Wet-Air Oxidation (WAO), with a third method, called Aggregation, as a backup. Each of these methods, however, is recognized to present significant technical challenges, so timely success is not assured.

In light of the importance of successfully resolving the TPB problem, in a way and on a time frame that supports overall SRS commitments for tank closure, WSRC recommended and DOE directed the establishment of a formal ITR to examine the problem and its planned resolution, to identify technical and programmatic risks, and to formulate recommendations to maximize prospects for success.

The ITR

The DOE approved ITR Charter is included in CBU-PIT-2006-00092 (Appendix 1). The Charter outlines the objectives of the Tank 48 ITR, the requisite size and composite capabilities of the ITR Team, the methods to be employed, and the evaluation time frame. Included in the Charter are nine lines of inquiry (LOI), addressing specific issues to be addressed by the ITR Team.

The Tank 48 ITR Team consists of eleven members, with extensive collective experience and capabilities applicable to the technical and management issues at hand. The Team includes extensive industry experience in chemistry, chemical engineering and nuclear management. Seven members are currently or retired senior scientists, engineers or executives. Four are university professors. Several members have had some professional involvement at SRS, but individually and collectively the Team fully meets the “independence” criterion established in the ITR Charter [CBU-PIT-2006-00092]. ITR Team members and their credentials are summarized in Appendix 2 of the report.

Key Conclusions

1. Previous WSRC Evaluations and Down-Selections

The first major element of the ITR was a retrospective assessment of prior WSRC evaluations of alternative means of processing the Tank 48 contents and selection of the current path forward. The ITR addressed the completeness of these prior evaluations, the treatment of risks and uncertainties, the stated and unstated constraints that influenced the evaluation process, and the validity of the ultimate selection of a path forward.

The ITR Team's over-arching conclusion, both in the retrospective assessment and in its broader examination of the overall Tank 48 path forward, is that while there has been a great deal of attention paid to TPB processing alternatives, that is only part of the problem. The WSRC evaluation and selection of TPB processing methods were thorough and led to sound conclusions, but have not fully addressed all of the issues necessary to achieve timely Tank 48 return-to-service.

The ITR Team concluded the two TPB processing methods chosen by WSRC as lead candidates (Steam Reforming and WAO) are technically sound, likely viable methods, and offer the best prospects for success among the approximately 80 alternatives considered.

However, the ITR Team also identified several areas in which the previous evaluations have not been sufficiently complete. As examples, heel management (removal of residual material and tank cleanup after removal of the bulk of the material currently in the tank), consideration of parallel-path options as outlined below, and understanding of the form, quantities, concentrations and implications of TPB processing by-products are all topics very important to success that received relatively superficial treatment in the alternative evaluations. These require further consideration, as delineated in this report.

2. Evaluation of Primary Treatment Process Options

The ITR Team examined the processing methods selected by WSRC as the primary and backup options, and several others. In the Team's view, the critical considerations for selection of a primary treatment technology include the (1) ability to produce a treated material compatible with subsequent vitrification at the Defense Waste Processing Facility (DWPF), (2) ability for the necessary process components to physically fit within the space envelope of the 241-96H facility (to avoid construction of a new radiation compliant building), and (3) process maturity to facilitate expeditious testing, design, construction and operation that is consistent to the extent possible with overall SRS schedule constraints.

Details of the ITR evaluations, conclusions and recommendations with respect to these technologies are provided in Section 4 of this report. The following is a summary of each.

Steam Reforming

Steam Reforming thermally reacts a high sodium content slurry and potassium TPB followed by oxidation of off-gases. The reaction takes place between solid and gas phases in a series of two fluidized beds, the first operating at 650-725°C and the second at 800-900°C (both at one atmosphere). Steam Reforming under the planned operating conditions will normally produce exhaust gas (predominantly CO_2, N_2 and H_2O) and a solid product (predominantly Na_2CO_3,).

Energy is provided to the fluidized bed reactors in the form of a solid fuel (e.g., coal), with residual fuel or carbon compounds potentially remaining in the solid product. The solid product then would be slurried through addition of water and transferred for blending with other wastes as feed for DWPF. Additional processing may be required if residual elemental and organic carbon in the solid product is not in sufficiently low concentration to meet limits imposed by DWPF processing requirements.

Steam Reforming is the most mature of the candidates, particularly for radioactive material applications, considering the advanced design work for Steam Reforming remote operations currently in-progress for treatment of sodium bearing tank wastes at Idaho National Laboratory (INL). Its processing products can most likely meet SRS needs.

Wet-Air Oxidation (WAO)

WAO aims to remove organic constituents from the same feed slurry through oxidation at lower temperature but higher pressure. WAO is typically operated at approximately 300°C and 100 atm. Oxygen or air is injected to the process, resulting in three phases within the reactor: gas, solid (from insoluble components in the waste feed), and aqueous solution.

The extent of oxidation of organic constituents depends on operating conditions, with residual organic constituents that may include benzene, phenol and acetates. The primary process effluents are exhaust gas and aqueous slurry. Aqueous slurry effluent from WAO may require further treatment if the concentrations of organic constituents exceed limits imposed by DWPF processing requirements.

WAO is a strong candidate, but it is less developed than Steam Reforming for this application and is lacking demonstrated performance in radioactive material processing. Its very high pressure operating regimen also poses a challenge. None of these obstacles is considered by the ITR Team to be insurmountable, but it is the Team's judgment that it would take longer (in comparison to Steam Reforming), by a year or more, to achieve WAO operational status at SRS.

Fenton's Reagent

Although not formally carried by WSRC as a prime candidate, the Fenton's Reagent process continues to be considered by many to be a viable, attractive candidate and for that reason, the Team included Fenton's Reagent in its review scope.

Fenton's Reagent uses a mixture of hydrogen peroxide and a ferrous iron catalyst at 1 atm. and around 95°C. The lower temperature and pressure are advantages counterbalanced by the use of potentially explosive peroxide. Fenton's Reagent produces only partial oxidation of the hydrocarbons; a substantial fraction of the hydrocarbons appears to be released at the start of the reactions as benzene.

Fenton's Reagent probably could be made to work. However, the large reactor volume, the high inventory of radioactivity in the reactor, the relatively sudden release of much of the available benzene, the increase in the waste volume, and the hazard of large-scale use of peroxide will be problems in the use of Fenton's Reagent technology. Therefore, processing using Fenton's Reagent is not recommended for further consideration.

<u>Aggregation</u>

Aggregation involves blending Tank 48 contents with other SRS process wastes to form a combined waste stream suitable for processing into Saltstone. Saltstone is made by blending the aqueous waste stream to be treated with a dry blend of Portland cement, blast furnace slag and coal fly ash to form a cementitious grout. The resulting material is pumped into an engineered reinforced concrete vault for disposal on-site. The grout cures to a monolithic, cementitious solid within the vault as the final waste form. Benzene-producing chemicals like TPB can be successfully incorporated into this structure.

Although the aggregation approach appears attractive from a schedule standpoint, the ITR Team understands that it is considered to be unacceptable as a bulk treatment approach by DOE[2] and the State of South Carolina, because it would effectively constitute disposal on site of a substantial amount of radioactivity (~400,000 curies of Cs-137). This is a matter of policy, not technical viability.

From a technical standpoint, use of aggregation would require upgrades to the Saltstone Production Facility (SPF) and disposal vaults to be compatible with potential benzene evolution during processing and curing from a flammability hazard perspective. In addition, the ultimate fate of the large quantity of benzene that may be evolved during (potentially long-term) degradation of TPB after placement in a Saltstone vault must be better understood. The primary ITR Team concern is the potential for new on-site groundwater contamination even if regulatory leaching criteria (e.g., TCLP) are met.

Recognizing these concerns, the ITR Team does not consider aggregation to be a viable approach for processing of the Tank 48 bulk material. However, it may be a viable back-up strategy if the policy considerations and concerns over the fate of benzene are addressed.

As a separate matter, the ITR Team considers Saltstone to be an appropriate treatment path for Tank 48 heel flush solutions because their curie and TPB content will be much, much lower than those for the bulk material.

[2] Per DOE letter SPD-06-150, Aggregation may be carried as a backup approach, and may be employed only if it is determined that neither of the primary options (SR and WAO) is viable.

Selection and Implementation of a Tank 48 Processing Technology

Based on the above, the ITR Team concludes that Steam Reforming is the preferred method for bulk treatment of the Tank 48 material, and work should continue, on a high priority basis, to confirm its viability, per the recommended actions in Section 4. WAO should be carried as a backup, but developed only to the degree necessary to confirm its technical viability.

As work proceeds, the ITR Team considers resolution of the following issues as essential to confirm and implement Steam Reforming as primary processing method and to carry WAO as a dependable backup:

- The criteria for compatibility of the treated Tank 48 wastes as a feed for DWPF must be clearly established. This includes, but may not be limited to, the acceptable forms and corresponding concentrations of organic and elemental carbon remaining in the Tank 48 wastes after treatment.
- Pilot-scale testing is need to demonstrate system operability with respect to fuel source and solid product that meets the defined requirements for subsequent feed to DWPF. In addition, preliminary design should demonstrate the compatibility of the Steam Reforming system, including necessary ancillary equipment, with the 241-96H facility space constraints.
- For WAO to be considered a dependable back-up, testing to demonstrate the system's ability to produce a slurry effluent that meets the defined requirements for DWPF should proceed as currently planned.

The Team does not consider it necessary to continue pursuit of any other processing methods. The current options are well understood and offer sufficient diversity and back-up with manageable technical and programmatic risks.

3. The Integrated Path Forward

Beyond its TPB processing component, the Tank 48 Path Forward must address other elements, as follows:

Pre-Concentration of Processing System Feed

The Team identified potentially significant advantages to concentration of the Tank 48 material prior to processing and/or temporary staging. The Tank 48 bulk contents could be concentrated by a factor of about three (from ~3wt% to ~ 10wt%) using well understood and readily available filtration systems. Increasing the concentration of the material to be processed would improve processing efficiency and shorten overall processing time, and it would also allow staging of the total quantity of Tank 48 bulk material in a substantially smaller tank (less than 100,000 gallon capacity).

Because concentration of the feed would also increase specific curie content of the processing system feed, this approach would demand careful analysis and engineered and/or operational controls to preclude violating total inventory limits for the processing system facility. However, in view of the potentially significant benefits of concentration, the Team recommends that it be given strong consideration.

Heel Management

Heel management - the sequence of tasks necessary to remove the residual material (the bottom ~2") from Tank 48 after bulk material removal, followed by tank flushing and cleaning to render that tank suitable for reuse - presents both significant technical challenges and uncertainties. Moreover, it is the last major step on the critical path to tank release, and therefore the potential adverse schedule impact of risks and uncertainties is magnified.

The ITR Team recommends that heel removal and tank cleaning be accomplished by means of a flushing regimen involving an initial series of water flushes, followed by a second series of flushes with salt solution chemically similar to the solutions to be reintroduced to the tank after it is returned-to-service. Depending on the observed effectiveness of those flushes, a third flushing step, utilizing stronger chemical cleaning solutions, may also be necessary.

For this heel management approach, effluent liquids from the initial water flush will be collected for treatment via the same system (Steam Reforming with pre-concentration) to be employed for bulk TPB processing. Based on the expectation that concentrations of Cs-137 and TPB will be very low, the ITR Team recommends that subsequent flushes be treated and disposed via Saltstone.

A central element to successful heel management is the establishment of end point criteria for Tank 48 cleanliness that are appropriately conservative (in terms of effects of tank residuals on down-stream receivers) and practically achievable. To that end, the ITR Team proposes a fundamentally new end point model wherein the tank could be accepted for return-to-service based on demonstration that TPB concentration in salt solution flush effluents are lower, with substantial margin, than levels that could cause flammability or other problems for downstream processes.

ITR assessment, conclusions and recommendations regarding heel management and regarding pre-concentration of feed are presented in Sections 5 and 6 of the full report.

Parallel Path vs. Sequential Processing

In concept, the best opportunity for achieving the January 2010 need date for Tank 48 return-to-service would be to take the TPB processing task - a multi-year duration activity involving significant technical challenges and uncertainties - off the critical path. This could be achieved by transferring the bulk tank contents from the tank as soon as possible to a different receptacle (one or more tanks) that would serve as the feed system for subsequent processing. From that point, the heel removal and tank cleaning activities could proceed independently and in parallel with the TPB processing work.

In comparison with the current sequential processing strategy, the parallel path approach offers high potential for both schedule acceleration and schedule risk reduction - but it would require a technically suitable interim storage location for the TPB-laden waste material currently in Tank 48. Such a location is not readily available.

Previous SRS evaluations have concluded that such an approach would not be cost or schedule effective. The ITR Team believes otherwise.

There are two possible avenues for staging of Tank 48 bulk material prior to processing: adaptation of an existing tank (Tank 24[3] appears to be the best candidate) or construction of a new tank. If the new tank approach were selected, the tank would be located and designed for safe interim handling of the TPB-contaminated Tank 48 waste, for feed to the TPB processing facility, and for subsequent cleaning - and it could be pre-designated for other use (probably SWPF feed) following TPB processing. Neither approach would be easy and either would involve incremental costs higher than the current sequential strategy. But both are feasible, and in the ITR Team's view either could be accomplished on a faster schedule and with reduced schedule risk than the current approach.

Section 6 of the report presents the ITR assessment, conclusions and recommendations with respect to the parallel path approach.

The Bottom Line: ITR Recommendations for Resolving the Tank 48 Problem

The central objective of the SRS Tank 48 path forward is to return the tank to service in time to support the *FY06-FY12 Liquid Waste Disposition Processing Plan*, (DPP) schedule, which is, in-turn driven by FFA commitments for SRS tank closure. The DPP calls for availability of Tank 48 by January 2010.

[3] Tank 24 is a Type IV tank. Although it is an older style tank without full containment, its condition, location and tank farm interconnections make modification and reuse feasible.

In the Team's collective judgment, January 2010 is not realistically achievable by the sequential processing approach currently envisioned by WSRC, utilizing either Steam Reforming or WAO as a primary processing technology. With sequential processing, it is very unlikely that Tank 48 can be returned-to-service any sooner than early-to-mid 2011, and delay by an additional year or more beyond that timeframe is quite possible.

Recognizing that plans for HLW processing involve some inherent unpredictability, it may be possible to meet IPP objectives with a Tank 48 return-to-service a year or more later than the currently projected need date of January 2010. The Team is not in a position to judge the implications or acceptability of a schedule slip of that magnitude; WSRC and DOE management must make that call based on regulatory, stakeholder and other programmatic considerations.

Based on the constraints of the established schedule and the Team's conviction that the current WSRC plan is unlikely to achieve that schedule, the ITR Team recommends that the parallel path be adopted. And noting that except for significant schedule risk, the current plan is viable. The Team also offers an alternative recommendation for DOE and WSRC management consideration, should they be willing to accept that schedule risk.

In summary, the ITR Team recommends a Tank 48 Path Forward, as follows:

1. Regardless of strategy (sequential or parallel path):

   - Commit to Steam Reforming as the lead TPB processing approach, now; carry WAO as the backup processing approach, and conduct work as necessary to confirm viability of WAO (but no further, so as not to dilute the effortto implement Steam Reforming). ITR recommendations for Steam Reforming and WAO development and testing, consistent with this overall recommendation, are provided in Section 4 of the report.

   - Embark on high priority heel management project, including development, testing and planning for tank flushing, and establishment of a revised TPB acceptance criterion for tank return-to-service, both as outlined in Section 5 of this report.

   - Conduct a high-priority evaluation of merits and methods for pre-concentration of Tank 48 bulk; establish a pre-concentration sub-project accordingly.

2. To maximize the chances of achieving Tank 48 return-to-service by January 2010:

   - Adopt the parallel path approach outlined in Section 6 of the report.

   - Embark immediately on a high priority project first to select the optimal feed tank system (i.e., modification of an existing tank or construction of a new one), and then implement that selection. This project will become the controlling activity on the critical path to Tank 48 return-to-service. Manage it accordingly.

- Continue to develop and implement the Steam Reforming for TPB processing on the earliest practical schedule (to preclude the bulk Tank 48 material from becoming an "orphan" waste).

3. Alternative recommendation, if returning Tank 48 to service a year or more later than January 2010 is considered tolerable by DOE and WSRC management:

   - Continue with the present course (sequential strategy), with resource allocation and project management actions directed to addressing the Steam Reforming technical and programmatic risks and accomplishing the development work needed for rapid implementation of Steam Reforming at SRS, as outlined in Section 4 of this report.

In summary, the ITR Team is confident that the TPB-contaminated HLW currently in Tank 48 can be safely and successfully removed and that the tank can be returned-to-service. The actions needed to accomplish these tasks are well understood and fully within the capabilities of WSRC. The most daunting element of the job will be to meet the schedule constraints currently in place.

The ITR Team has offered its best judgments as to how to accomplish the established technical and programmatic objectives. Full details on the ITR assessments, conclusions and recommendations of the ITR Team are available in the balance of this report.

1.0 Introduction & Background

The ITR Team convened at SRS on June 6, 2006, for the purpose of evaluating the WSRC path forward for resolving the problems resulting from TPB contamination in Tank 48[4].

This is a report of the ITR Team's evaluations, conclusions and recommendations. It includes an explanation of the technical issues involved, the Team's independent assessment of WSRC work completed to date, and the Team's conclusions regarding the viability of the current path forward and recommendations as to actions that can protect or improve overall prospects for success.

1.1 Brief Background on the Problem

In-Tank Precipitation

Beginning in 1983, the ITP process was developed, tested and ultimately chosen as the primary method for SRS HLW salt processing. ITP involved addition of sodium tetraphenylborate (NaTPB) into a HLW tank in order to capture and convert the radio-cesium in the tank into a solid precipitate, which could then be readily separated and removed from the liquid waste.

In December 1995, following the first large scale application of the ITP process, benzene emission rates from the processing tank (Tank 48) were found to be much higher than expected, posing a flammability hazard at points of possible gas accumulation such as the tank head space. Extensive subsequent technical evaluations determined that the benzene releases were caused by in-tank catalytic reactions, at elevated temperatures and in the presence of palladium and other catalysts. Based on this finding and WSRC's inability to establish a safe and predictable ITP operating envelope, the process was suspended in 1998. That suspension remains in effect.

As a result, the Tank 48 contents (~250,000 gallons of salt waste) are contaminated with nearly 22,000 Kg of organic TPB compounds. Tank 48 is a large new-style[5] tank in the SRS H-Tank Farm (HTF) that is needed to support management and processing of SRS HLW. But the TPB contaminated salt waste must be removed before the tank can be returned-to-service.

[4] The tank's full designation is 241-948H, indicating its presence in the H Area Tank Farm. For simplicity it is referred to in this report as "Tank 48"

[5] Tank 48 is one of 27 Type IIIa tanks, the newest vintage of SRS HLW tanks, characterized by double-shell configuration providing full secondary containment for leak protection.

There have been numerous evaluations in the intervening years of methods to deal with the Tank 48 problem. The most recent WSRC evaluation of alternatives, completed in April 2006 [G-ADS-H-00011], identified Steam Reforming, WAO, and Aggregation as the preferred methods for treatment of the Tank 48 material. The May 2006 Department of Energy-Savannah River (DOE-SR) letter regarding Tank 48 Recovery [SPD-06-150] directs that the Aggregation method be reserved as a back-up approach, for use only if the other methods prove unworkable. These three methods - Steam Reforming, WAO and Aggregation (as a back-up) comprise the current WSRC path forward and are the major subject of the ITR evaluation.

1.2 The Independent Technical Review

Objectives

The overall objective of the ITR was to confirm the viability of the current WSRC path forward for Tank 48. As part of this objective, the review was intended to identify technical and programmatic risks and uncertainties with the selected path, and to determine if these have been thoroughly examined and countered with effective mitigation strategies.

This objective was refined in the form of nine specific LOIs articulated in the official charter Rev. 2, for Tank 48 ITR [CBU-PIT-2006-00092, Appendix 1]. In summary, these are:

1. Validate completeness of Tank 48 alternatives evaluation.
2. Evaluate the treatment of constraints.
3. Evaluate the treatment of technical and programmatic uncertainty.
4. Validate the down-selection process employed in previous evaluations.
5. Assess the viability of the selected technologies and current path forward.
6. Identify risks and assess adequacy of risk management actions.
7. Evaluate dissolution of the K-TPB, to facilitate its processing.
8. Evaluate plans for Tank 48 cleaning and heel management.
9. Evaluate plans and practices for benzene management.

The ITR Team

Members of the ITR Team and their credentials are summarized in Appendix 2.

In composite, the 11-member ITR Team comprises expertise and extensive experience in design, engineering and management of chemical processing and radioactive waste management systems. The experts are independent of any corporate accountability or responsibility for managing Tank 48 return-to-service or for selection of the preferred technologies, and are free of conflicts-of-interest with respect to potential benefit from the selection of any specific technology.

ITR Methods and Process

To accomplish its objective, the Team reviewed existing documentation of SRS Tank 48 evaluations (with particular attention to the comprehensive Systems Engineering Evaluation (SEE), *Tank 48 Return to Service* [G-ADS-H-00011], attended briefings and follow-up interviews with WSRC and Savannah River National Laboratory (SRNL) personnel, visited the Tank Farm, observed configuration, operation and/or testing of Steam Reforming and WAO systems at other sites, and conducted numerous internal discussions. To facilitate its work, the Team was structured into several sub-teams to examine, in parallel, several key elements including the viability of the Steam Reforming and WAO processes, technical issues related to Tank 48 heel removal, and prospects for composite and/or decoupled solutions.

The ITR Team was directly engaged in the identification and definition of the Tank 48 problem. This was a conscious and important element of the ITR method, chosen to take full advantage of the capability and experience of the Team members and to help guard against prematurely or excessively narrowing the review. As an example, the ITR Team added three LOIs to the set included in the original approved charter.

The ITR work was conducted on an aggressive schedule, commencing in early June and completed (with the issuance of this final report) on August 10, 2006.

2.0 The Tank 48 Problem - and its Possible Solutions

Based on current plans, Tank 48 will be needed for salt waste processing in early 2010. The importance of the tank for future waste processing is not just its large capacity, but its material condition and configuration (that is, a new style tank with full secondary containment), and its location and interconnections within the HTF. It is a component that is essential to preparing feed for the Salt Waste Processing Facility (SWPF) at a rate which would allow that facility to operate at design capacity, upon commencement of radioactive operations (now scheduled for 2011).

2.1 The Problem Defined

The tank currently is less than 20% full, but its contents include approximately 21,800 Kg of Cs/KTPB, which releases benzene and thus can create a potentially flammable condition in the tank vapor space. Agitation of the tank contents increases the quantity of benzene released, and for that reason it is SRS practice to blanket the tank vapor space with nitrogen when the tank contents are being agitated. The tank contains approximately 430,000 curies of Cs-137 and lesser amounts of other radionuclides. Because of the TPB content and its associated flammability risk, the tank has been isolated and transfers to and from it are currently prohibited.

Solving the Tank 48 problem involves two distinct and separable tasks:

1. Removal of the bulk contents from Tank 48 and then cleaning the tank for return-to-service.

2. Processing Tank 48 contents to eliminate the TPB hazard, and then disposing of the waste products.

Cleaning the tank will require a series of flushes, and possibly chemical cleaning. Processing the tank contents will require destruction of the TPB and removing organic carbon from the slurry, prior to vitrification of the radioactive waste product in DWPF.

Based on current processing plans, if Tank 48 is not returned-to-service for salt waste processing by January 2010, SRS will not have enough HLW tank space to meet its commitments on HLW tank closures, DWPF glass canister production, and staging waste salt feed for the SWPF.

Tank 48 Configuration

Tank 48 is a 1.3 million gallon, Type IIIa underground HLW tank. It is approximately 85 ft. diameter by 33 ft. high (Figure 2-1).

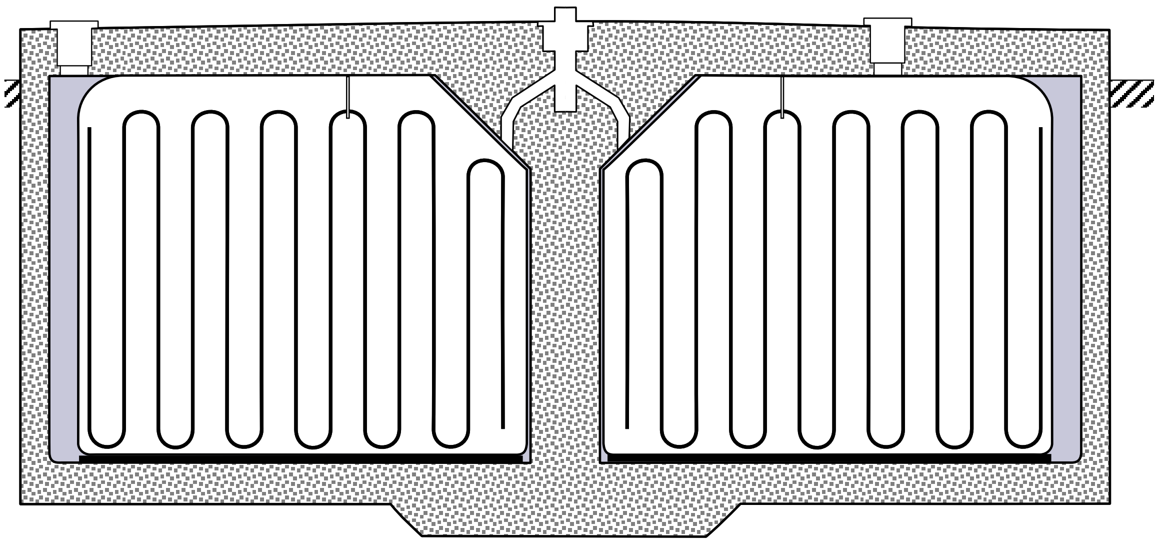

Figure 2-1: Schematic of Tank 48

The tank was designed to store HLW from the two processing canyons at SRS and contains approximately four miles of piping for cooling coils. There is also a large number of piping supports and other physical obstructions in the tank. The presence of all of these obstructions will create challenges to cleaning the tank effectively.

The tank contains approximately 250,000 gallons of slurry, of which approximately 3wt% are in solid form. The solids are composed mostly of Cs/KTPB along with a small amount of monosodium titanate (MST) and sludge. The density of the solids is near the density of the liquid, which could facilitate cleaning of the tank.

Tank 48 Radiological Contents

The radiological characterization of the tank contents[6] is summarized in Table 2-1. Initially (that is, after introduction of NaTPB into the tank during ITP operations), >99.99% of the Cs-137 was in the solid phase. Approximately 3% of the Cs-137 has subsequently redissolved due to radiolytic and chemical degradation of the TPB.

	Total Curies	**Soluble Curies**
Cs-137	430,000**	12,000 (~3% of total)
Sr-90	310	NM
Total Alpha	1,500	NM
	Total Grams	**Soluble Grams**
Tc-99	NM	2,150
Total U	6,000	5,700
Np-237	270	50
Total Pu	130	20

NM=Not Measured

* Extracted from Table 1, CBU-PIT-2005-00046, page 3.

** Some discussions with WSRC included the curies from Ba-137m, which has a 2.6 minute half-life. The ITR believes this to be overly conservative.

Table 2-1: Tank 48 Radionuclide Characterization Summary*

Tank 48 Chemistry

Potassium Tetraphenylborate (KTPB) is a major chemical constituent that degrades and generates benzene, and is the prime target of a TPB destruction process. The phenylborates, phenol, and biphenyl are also degradation products of TPB and must also be destroyed. The fate of mercury in any TPB destruction process is also important and must be well understood. None of the other constituents present any particular concerns during TPB processing.

[6] Tank 48 radionuclide and chemical characterization has been detailed in SRS reports, CBU-PIT-2005-00046, Revision 1, *Tank 48 Radionuclide Characterization*, and CBU-PIT-2005-00066, Revision 2, *Tank 48 Best Estimate Chemical Characterization*. This provides a baseline of information for the overall 250,000 gallons of HLW in the tank, as used in this report.

Constituent	Total Kg	Soluble Kg
TPB Potassium Tetraphenylborate	19,400 21,800 (calculated)	<10
Triphenylborate	150	<10
Biphenylborate	130	<10
Phenylborate	140	<10
Phenol	890	670
Biphenyl	580	<10
Benzene	510	<10
Mercury	20	0.06
Boron	940	420
Potassium	2,400	240
Iron	150	<10
Aluminum	2,100	2,100
Sodium	67,500	66,000
Acetate	400	400
Oxalate	970	970
Nitrite	19,300	19,300
Nitrate	12,100	12,100
Phosphate	460	460
Hydroxide	21,000	21,000

*Extracted from Table 1, CBU-PIT-2005-00066, page 3.

Table 2-2: Tank 48 Chemical Characterization Summary*

TPB Description and Behavior

TPB consists of a boron atom bonded to four benzene molecules (Figure 2-2).

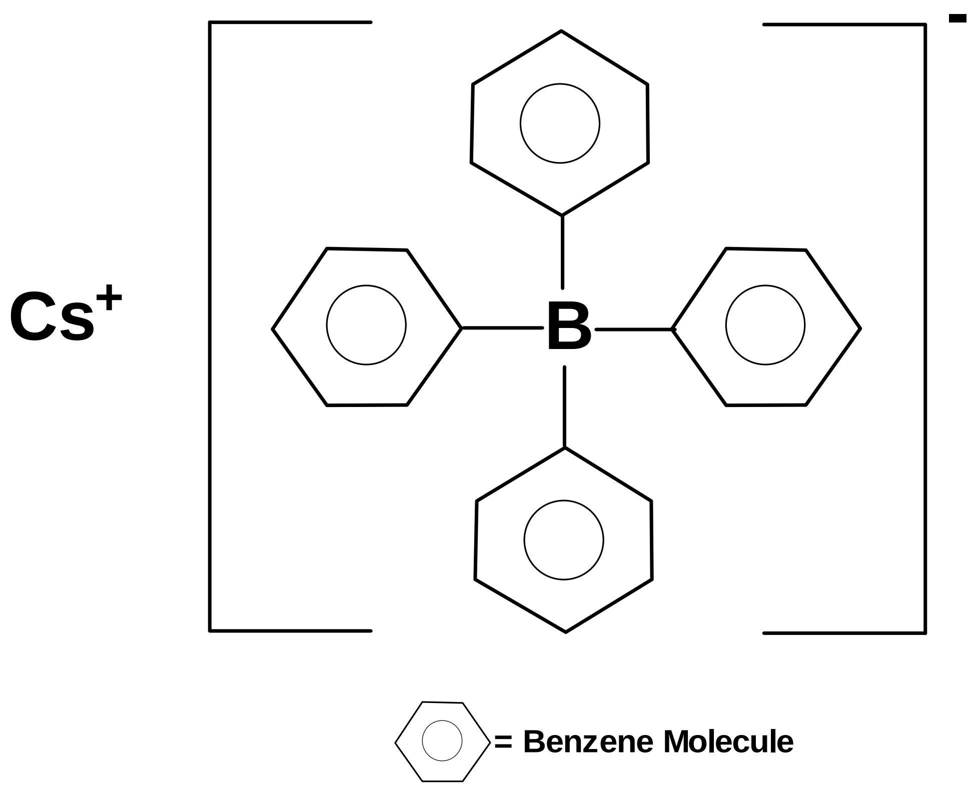

Figure 2-2: Cesium Tetraphenylborate Schematic

In Tank 48, TPB degrades in the presence of radiation and low concentrations of certain catalysts, such as palladium and copper. This is the source of benzene in the tank vapor space. Over the last 23 years, approximately 3% of the Cs-137 has been released from the TPB precipitate due to this degradation

When the TPB is removed from Tank 48 and processed for disposal, benzene will be generated by the mechanisms described above. Precautions must be taken at every process step to avoid flammability issues.

Similarly, if the TPB disposition process does not fully remove or destroy the benzene (as would be the case for example if aggregation were the chosen method) it must be assumed that benzene will be released into both the gas and liquid phases. Mitigating steps must be taken to ensure that no adverse environmental or safety issues result from these releases.

2.2 Potential Solutions

As noted in Section 2.1, solving the Tank 48 problem includes two distinct elements: (1) emptying Tank 48 and restoring it to a condition suitable for reuse, and (2) processing the tank contents in a way that eliminates the hazard and satisfactorily disposes of residual waste products.

For each element, there are several alternative courses of action and attendant choices and design decisions. While these will be discussed in detail in subsequent sections of this report, the following paragraphs describe the overall range of alternatives.

Bulk Material Removal

The first fundamental decision regards the path for removal of TPB from Tank 48. The current WSRC baseline plan is essentially a sequential approach, in which the Tank 48 material is removed and processed in a single step. After all of the bulk material is removed, heel removal and tank cleanout can commence, and when completed the tank can be returned-to-service. This approach is simple and straightforward, and it does not require large volume interim storage, but it places TPB processing, with its risks and uncertainties, on the critical path.

An alternative approach is to move the bulk material to a different receptacle (one or more tanks), which would serve as the feed system for subsequent processing. From that point, the tank could be cleaned and prepared for reuse, independently and in parallel with the material processing work. This "parallel path" approach essentially disconnects the two problem elements and offers potential schedule advantages and schedule risk reduction by removing TPB processing from the critical path of actions needed to return the tank to service. However, it would require a technically suitable interim location for the TPB-laden waste material currently in Tank 48, and such a location is not readily available.

The parallel path approach and its implications are discussed in Section 6 of this report.

Pre-Concentration of Bulk Material

As a related matter, the ITR Team examined the potential attractiveness of concentration of bulk material removed from Tank 48, in advance of processing. Concentration by a factor of approximately 3-5 would be achievable at relatively low cost using readily available filtration equipment.

Potential advantages of front-end concentration are (1) substantial reduction of the interim storage space needed to support a parallel path scenario, and (2) improvement in efficiency and total duration of processing, as a consequence of feeding a higher concentration material. However, for some processing scenarios, concentration could be disadvantageous - for example, if it were to increase the radioisotope inventory in 241-96H to the point that would exceed allowable for Hazard Category 3, the current 241-96H classification.

The issue of concentration is addressed in Section 6 of this report.

Heel Removal

After the bulk of the contents are removed from the tank, a small amount of the material will remain – the heel. Several flushes of water and salt solutions, plus a possible chemical cleaning, will likely be required to clear enough of the TPB from the tank for it to be ready to use as a salt processing tank. A disposition path for the flush material must be selected. It is likely to be impractical - and very possibly unnecessary - to process all of these flush solutions through a TPB destruction process. The best option for these materials is likely to be disposition via Saltstone. With an appropriate flushing sequence, the residual material to be disposed of by this method would include <10% of the Cs-137 currently in the tank.

Heel management is discussed in more detail in Section 6.1.

Dealing with Carbon

Satisfactory processing and disposition of the tank contents requires that >99% of the organic carbon be separated from the bulk of the tank contents. This is required so that the radionuclides can be processed through the DWPF, which can accept only very low levels of organic carbon.

Aqueous chemical processes using mild catalysts and modest temperatures can typically separate 30-50% of the organic carbon from the radionuclides. High-temperature, high-pressure, or processes that use strong oxidizing agents are typically required to achieve >99% organic carbon removal. In these more aggressive processes, the organic carbon is removed mainly as carbon dioxide.

Section 4 discusses in detail three processes being considered to achieve this destruction target. These processes are Steam Reforming, WAO, and Fenton’s Reagent.

Benzene Management

Early in its review, the ITR Team observed that SRS practices with respect to prevention of flammability conditions in areas of possible benzene vapor release (for example, in Tank 48 head space) are very conservative in comparison with U.S. chemical (non-nuclear) industry practice. SRS Tank 48 preventive measures include a high capacity, safety grade, redundant system, with instrumentation and controls, to inert the tank head space under all conceivable normal and emergency conditions. That system involves high capital cost, significant operations and maintenance expense, operator training, procedural controls and the like.

After brief examination, however, the Team confirmed that the SRS provisions properly reflect DOE requirements and expectations. On that basis, the Team chose not to pursue reduction of benzene management controls as a part of the solution to the Tank 48 problem.

2.3 The Ideal Processing Solution, in Concept

The ITR Team developed a view of an "ideal solution" to the Tank 48 problem. While this is a hypothetical solution only, the Team considered it useful as a frame of reference for evaluation and comparison of the various alternatives under consideration.

To be acceptable, any process of course must meet essential criteria such as compliance with DOE safety standards, acceptability to stakeholders (including DOE, Defense Nuclear Facility Safety Board (DNFSB), SCDHEC, and the general public), tolerable costs, etc. Beyond these, however, there are attributes considered to be important by the ITR and which collectively define the "ideal solution". These are:

- Processing products that can be seamlessly integrated back into the Tank Farm and that are fully compatible with DWPF feed limitations (e.g., with >99% separation of the carbon from the Cs-137)
- A physically compact process compatible with spatial and inventory constraints of the 241-96H facility
- An aqueous process
- A low-pressure process (< 100 psi)
- A moderate-temperature process (< 200 degrees C)
- A continuous process (vs. a batch process)
- A process based on fully demonstrated technology

- Throughput that allows completion in a reasonable period of time (1-2 years after startup)

- A process that produces no significant air-quality problems and that results in minimal increase in secondary waste to DWPF

- One that can accept >10wt% slurry feed, for efficient operation

3.0 WSRC Evaluations To-Date

The first major segment of the ITR Team's work (defined in LOI-1, LOI-2, LOI-3 and LOI-6) relates to the WRSC assessments of Tank 48 alternatives, as conducted over the past five years. Section 3 summarizes the ITR Team's retrospective review of this WSRC work and the Team's conclusions and recommendations in that respect.

3.1 ITR Retrospective Review

Retrospective Review Process

Prior to the initial ITR Team meeting on June 6, 2006, copies of the four major WSRC evaluations of Tank 48 options [G-ADS-H-00011, CBU-PIT-2005-00147, G-ADS-H-00007, WSRC-RP-2002-00154] and the report of a related risk analysis performed in 2005 [Y-RAR-H-00057] were provided to all Team members for review. This is a substantial compilation of material - totaling more than 500 pages.

At SRS, on June 6 and 7, 2006, the Team discussed these references and were briefed by WSRC and SRNL staff members on the HLW processes at SRS, on the Tank 48 problem and its genesis, on various areas of research performed and its results, on the various options considered over the past five years, and on the current path forward. The Team also toured the HTF.

Based on this composite information, on June 7th the entire ITR Team collectively conducted a qualitative comparison of all of the options previously considered. The Team used, as a starting point for this review, the "Crosswalk" tabular compilation of all previous evaluations [CBU-SPT-2006-00098].

The Team established several ground rules and criteria for this review, as follows:

1. Obviously similar or equivalent options (e.g., the same process applied in several different locations) would be considered together.

2. Each option, or similar set of options, would be considered for suitability by the ITR Team against the criteria in Table 3-1.

Criterion	ITR Consideration
Schedule	Potential of the given option to achieve Tank 48 return-to-service in the approximate time frame required (i.e., by 1/2010). Note that this was a qualitative Team judgment, based on collective experience of the ITR members.
Cost	Cost implications of the given option, rated qualitatively as "very high" or not, based on ITR collective experience and judgment.
Confidence in Success	A key technical judgment by the Team, related solely to the technical viability of the given option, based on experience, proven performance and scientific principles.
Regulatory & Permitting	Potential for success (or relative difficulty) with respect to achieving the approval and/or required permits from regulatory and oversight organizations.
SRS Process Compatibility	Anticipated compatibility of the option under consideration with existing or planned SRS HLW processing and handling systems, including Tank Farm operations, salt stone, MCU, SWPF and DWPF.
Physical Practicality	System and spatial implications of the proposed option, with particular attention to compatibility with space available in 241-96H and other locations proximate to Tank 48, as well as the potential requirement for complex systems, structures or equipment.
Real Safety	Anticipated safety issues of significance, such as those related to system pressure, temperature, emissions, toxicity or other dangers associated with chemical additives, and the like.
Other	Any other option-specific consideration deemed important by the Team.

Table 3-1: Assessment Criteria

3. Based on the above evaluations, the Team reached a consensus rating, in one of three categories (Table 3-2).

A	High-potential candidate. Deserves further consideration
B	Possible candidate, with resolution of some significant issues. Do not pursue actively at this time
C	Low-potential candidate. Take no further action

Table 3-2: Rating Categories

4. For cases in which an option was clearly not feasible (as agreed in Team discussion), it was rejected without further discussion and not included in the final compilation of results.

Following tabulation of results, the Team spent several hours reviewing the tentative conclusions, challenging them internally, comparing outcomes against the current path forward, and discussing the four LOIs (1-3 and 6) applicable to this exercise.

ITR Team Conclusions from Overall Comparison of Alternatives

The results of the ITR Team's evaluations are shown in tabular form in Appendix 3. From this, several overall conclusions are evident:

- The three approaches currently being carried by WSRC as primary (Steam Reforming and WAO) and backup (Aggregation) were all viewed by the Team as "A" candidates.

- Two options currently considered by WSRC to be feasible, but not currently being developed, were also considered by the ITR Team to merit "A" ratings. These are oxidation (Fenton's Reagent) and dissolution of potassium tetraphenylborate (KTPB). (These options, and the ITR Team's view of how they should be handled, are discussed in Section 4).

- As described in subsequent sections of this Report, it is the ITR Team's view that Aggregation is the only one of the options under consideration that is achievable with high confidence on the schedule required, utilizing the current sequential path approach.

The schedule complexities are further described in Section 6.

3.2 Completeness of Previous Evaluations

It was the consensus judgment of the ITR Team that the previous WSRC evaluations had considered and evaluated an adequately complete range of TPB processing alternatives. The eighty-two (82) alternatives in CBU-SPT-2006-00098 included several fundamentally different approaches and variants of many of these. The evaluations also included a variety of innovative approaches.

While other processing alternatives exist, for the purposes of selecting a viable means of removing the TPB from the Tank 48 HLW, the Team concludes that the WSRC evaluations were sufficiently broad and deep. Further, the Team did not identify any other processing options that should have been considered.

However, the ITR Team found the WSRC evaluations to be less than complete, in several respects. The evaluations did not fully address all elements of the Tank 48 path forward, such as the tank heel management and the possibilities and implications of concentration, and they did not thoroughly evaluate the alternative strategy of parallel path approach. Also, the evaluations did not fully address the implications of different TPB processing byproducts (particularly organic carbon), a very significant factor in the overall selection.

With respect to the tradeoffs between sequential and parallel paths and also the issue of heel management, the Team notes that WSRC evaluations identified some of the alternatives as “partial solutions” and in that sense recognized that multiple steps would be involved. But in the Team’s view there was generally inadequate attention to composite solutions or combinations of methods or processes needed to achieve the earliest possible resolution of the Tank 48 problem. In particular, the parallel path approach was not examined thoroughly.

Disposition of the tank heel following removal of bulk material from the tank was generally not addressed. This activity is common to all processing options, and therefore arguably not appropriate for evaluations of alternatives. Nevertheless, the ITR Team considers this to be a fundamental element of a successful path forward and therefore one which requires substantial attention.

As addressed in detail in Section 4, the form and quantity of carbon byproducts of TPB processing are very important considerations in selection and design of a TPB processing system. Because of the demanding Waste Acceptance Criteria (WAC) for DWPF, the objective of merely destroying the TPB is not adequate - most forms of carbon need to be removed in order to prevent problems with the DWPF melter. This matter was not comprehensively covered in the WSRC evaluations.

In short, the WSRC evaluations were quite complete in identifying and comparing TPB processing alternatives, and as noted in Section 3.5, they enabled a technically sound down-selection - but they did not fully examine all of the elements of Tank 48 path forward.

3.3 Treatment of Constraints

ITR Review of Constraints

In reviewing the four prior WSRC alternatives evaluations, and even more so in discussing these evaluations with WSRC staff during the briefings during the week of June 5th, members of the ITR Team noted numerous instances in which judgments regarding the suitability of various options were influenced by constraints, some stated and some implied. Concern regarding the potential significance of such constraints, and particularly the unstated ones, led the Team to establish new LOI-6. (See Section 1).

The ITR Team considers the treatment of constraints to be important both in terms of possible influence or bias in previous evaluations and down-selections of Tank 48 alternatives, and with respect to future Tank 48 work and the effects (and unintended consequences) such constraints may have.

Regarding the retrospective evaluations (as described in Section 3.1, above), documented constraints (or assumptions) included in Table 3-3.

Category	Documented Constraint	Implications
Schedule	The ability to meet the schedule requirement accepted at the time was a defined screening or evaluation criterion in the three most recent treatment technology evaluations [G-ADS-H-00011, CBU-PIT-2005-00147, G-ADS-H-00007] and the 2005 Risk Analysis [Y-RAR-H-00057].	Over time, the need date for Tank 48 return-to-service has varied, based on changing disposition plans, better or worse system performance than expected, changing HLW backlog. Therefore, prior selections or rejections based on schedule implications may have been premature.
Cost	The relative cost of each treatment option was a defined screening or evaluation criterion in the three most recent treatment technology evaluations [G-ADS-H-00011, CBU-PIT-2005-00147, G-ADS-H-00007] and the 2005 Risk Analysis [Y-RAR-H-00057].	The annual and cumulative costs to manage Tank 48, to handle, transfer and process the contained material, and to clean and return Tank 48 to service will be very high. Also, consequential costs (such as possible effects on DWPF waste loading) can also be high. Rejecting any viable alternative based on cost could lead to rejection of an otherwise preferred candidate.
Permissible residual TPB	It was initially presumed that for Tank 48 reuse, residual TPB must be less than 378 grams - an amount essentially impossible to detect.	While this constraint has not influenced the previous WSRC evaluations (because post-processing cleanup was assumed to be needed in all cases), this is a very significant constraint in terms of affecting the time and cost of Tank 48 return-to-service. The most current documented criterion for Tank 48 Return-To-Service is that the TPB content must be 35 Kg or less [CBU-SPT-2005-00177]. The ability to confirm even this quantity of material in the heel of a tank 85-feet wide is a technical challenge.
Residual radioactivity in South Carolina	Per DOE direction [SPD-06-150], the Aggregation option is limited to backup role, to be employed only as a last resort. The primary reason for this restriction is concern by the State of South Carolina regarding residual curies in the state.	As described in subsequent sections, the Aggregation approach is considered by the Team to have strong potential, both as a primary means of processing the Tank 48 material and as a means of dealing with the tank residual, post-transfer.

Table 3-3: Documented Constraints

In addition, presumed constraints that appear to the ITR Team to have been widely accepted but not documented, are listed in Table 3-4.

Category	Presumed Constraint	Implication
Addition of organics to Tank 48	There can be no significant addition of organic material to Tank 48	Options involving addition of significant organics, such as solvents to dissolve the KTPB, were rejected as infeasible. This single presumed constraint precludes numerous, potentially attractive, alternatives.
New Tanks	No new waste tanks can be built at SRS	This has been a long-standing stakeholder expectation, but it could be the key to a parallel path option, and has not been fully explored. The ITR Team notes that a new processing feed tank, as distinct from a waste tank, could be very useful.
Benzene Handling	Current Tank Farm handling practices and restrictions (e.g., with respect to inerting, monitoring, allowable concentrations, etc.) must be carried forward for all tank operations involving benzene.	Common practices proven to be effective and safe in the chemical industry have not been considered for use at SRS, and could open up opportunities for more practical handling.
Temporary Reuse of a Type IV Tank	No Type IV Tanks can be used to temporarily store waste currently in Tank 48, or any intermediate or final product of processing of the waste in Tank 48.	This has been a long-standing informal commitment to stakeholders. It will be addressed in formal commitments that are negotiable if the stakeholders were to be made confident if the temporary use of the appropriate Type IV Tank was indeed temporary, and for a single campaign (best demonstrated by a parallel project to treat the waste).

Table 3-4: Presumed Constraints

Conclusions and Recommendations Regarding Constraints

By definition, constraints limit the range of possible remedies to the Tank 48 problem. Given the evident difficulty WSRC has had in achieving success in this area, very close attention to constraints and their implications is warranted.

In the ITR Team's view, neither the documented nor the unstated constraints have been treated with sufficient rigor in the existing evaluations, and ambiguity in this regard may unnecessarily (and unintentionally) foreclose otherwise tractable solutions. The ITR Team believes that particular attention needs to be paid to the unstated constraints. These can unintentionally bias the down-selection, analysis and engineering processes in ways that are inconsistent, unjustified and difficult for oversight/management to detect.

Recommendation 3-1:

For all ongoing and future work, establish a "constraint register" in a manner consistent with current practice vis-à-vis "risk register". In the Constraint Register, identify the constraint and its basis, and define the specific nature and limits of its application.

3.4 Uncertainties and Risks

ITR Review of Uncertainties and Risks

In the course of its review of the four prior WSRC evaluations of Tank 48 treatment technology alternatives, the ITR Team considered how uncertainties and risks were treated in these evaluations. The Team found a great deal of variability with respect to risk and uncertainty treatment. In some cases, most notably, the development of the aggregation approach, WSRC performed a full and methodical risk assessment, including the development of a risk register. In other cases, it was clear from discussions with participants and from the text of the various alternative reviews that risks and uncertainties were consciously included in the evaluation process, if not formally documented. And in many cases, alternatives were screened out, justifiably, with no evident attention to risks and uncertainty, because in those cases the alternative was considered not viable.

Given the general confirmation by the ITR Team of the completeness and effectiveness of the WSRC evaluations of processing alternatives, the Team concluded that the somewhat inconsistent treatment of risks and uncertainties did not lead to improper selection of processing methods.

Conclusions Regarding Uncertainties and Risks

Uncertainties and risks were considered with adequate thoroughness to support conclusions with respect to processing technology selections, but not adequately to focus attention on the fundamental schedule risk posed by the entire path forward.

3.5 Validity of Evaluation Process

The ITR Team's assessment of the validity of the WSRC evaluation of alternatives was an implicit part of the Retrospective Review, described in Section 3.1 above.

In summary, given the Team's conclusions as noted in the sections above that the evaluations were reasonably complete, that the specific processing options considered viable by the WSRC staff were also selected by the ITR Team, and that the Team considered the treatment of constraints, uncertainties and risks to be adequate, it can be concluded that the overall WSRC Evaluation Process was valid.

As noted in the previous sections, the Team did identify areas of inconsistency (particularly regarding the changes in screening and evaluation criteria in the successive evaluations), the need for more methodical treatment of constraints, and to the inadequate focus on schedule risk. The Team concluded that these shortcomings did not lead to improper conclusions or actions regarding processing technology selections, but they may have led to an under-appreciation by WSRC management and staff of the schedule risk posed by the overall sequential processing strategy.

4.0 TPB Processing Technologies

This section presents the ITR Team's evaluations of candidate processes for treating the contents of Tank 48. The ITR examined processes that are part of the SRS current path forward (Steam Reforming and WAO), and other candidates considered to have high potential. The ITR evaluation assessed the suitability of each for treating Tank 48 wastes as primary treatment options prior to vitrification of the treated material in DWPF.

The Team also examined aggregation, a technology that would treat the Tank 48 waste by incorporation in saltstone, blended with other waste streams and ultimately remaining on-site at SRS as a cementatious waste form in concrete vaults. Aggregation is currently carried as a back-up technology, should the primary candidates prove to be unworkable.

4.1 Critical Considerations

Critical considerations for selection of a primary treatment technology include the (1) ability to produce a treated material compatible with subsequent vitrification at DWPF (including adequate removal of organic carbon), (2) ability for the necessary process components to physically fit within the space envelope of the 241-96H facility (to avoid construction of a new radiation compliant building), and (3) process maturity to facilitate expeditious testing, design, construction and operation that is consistent to the extent possible with overall SRS schedule constraints.

A major assumption that is important to this study is the amount of elemental carbon and organic carbon that can be present in the products of the decomposition reactions. The ITR has been given a variety of methods for estimating this limit, but the limit is likely to be set by either the flammability of benzene in DWPF or the level of redox reduction by residual carbon that could adversely impact the DWPF process chemistry. The redox potential in the melt is expected to be the limiting condition, and approximately 15,000 ppm of total organic carbon (TOC) was suggested as a reasonable limit for DWPF feed (however a substantial portion of the allowable TOC in the feed may be attributed to formic acid addition to reduce mercury as part of the DWPF processing).

A more clear definition of the residual elemental carbon and organic carbon requirements, as well as other conditions for compatibility with DWPF, is central to making appropriate process selection and design choices. In the absence of this needed clarity, carbon removal estimates are set at 99% , usually the removal that has been seen in early testing or removal that appears to be attainable. The Team considered removal in the range of values needed.

Technical details of the alternative processes are discussed in the following sections.

4.2 Steam Reforming

The Steam Reforming[7] process, marketed by THOR Treatment Technologies LLC (THOR)[8], is a candidate process to treat SRS Tank 48 TPB waste. In the THOR process, waste feed, superheated steam, and co-reactants are introduced into a fluid bed steam reformer vessel where liquids are evaporated, organics are destroyed, and reactive chemicals in the waste are converted to a stable waste product that incorporates the radio nuclides.

Steam Reforming has been used to treat highly radioactive waste. Studsvik has run a commercial Steam Reforming Processing Facility in Erwin, TN, since 1999 [WM-4529]. The Erwin Facility can process ion exchange resins, charcoal, graphite, sludge, oils, solvents, and cleaning solutions with contact radiation levels of up to 400 R/hr. Fluid bed operation, a significant part of Steam Reforming, is a mature technology and was employed in high radiation operations in the Calciner facility at INL for about 20 years.

The Steam Reforming technology has been evaluated or tested for remediation of the following:

- Hanford low-activity waste (LAW) into either carbonates or silicates that can subsequently be vitrified [WSRC-TR-2002-00317].

- Hanford LAW and SRS salt supernate into a final waste form (aluminosilicate mineral) for land disposal [WSRC-TR-2002-00317, PNWD-3288, WSRC-MS-2003-00595].

- INL SBW into a carbonate form acceptable to Waste Isolation Pilot Plant (WIPP) as a final waste form or into sodium aluminosilicate as a final waste form for land disposal [INEEL/EXT-03-00437].

- SRS Tank 48 HLW supernate with TPB into either carbonates or silicates compatible with subsequent vitrification in DWPF [WSRC-TR-2003-00352, WRC-MS-2004-00288, INEEL/EXT-03-01118].

- SRS Low-Curie and High-Curie salt supernates into carbonates, silicates, and sodium aluminosilicate mineral forms for burial at WIPP or Yucca Mountain [WSRC-STI-2006-00027].

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7 In this report, and in various references, the terms “fluidized bed steam reforming”, or FBSR, and “steam reforming” are used interchangeably.

8 THOR Treatment Technologies is an affiliate of the Washington Group International (WGI), the parent corporation of the leading partner of WSRC, the SRS prime contractor. The ITR Team was aware of that relationship. It did not influence the team’s evaluation in any way.

The SRNL has shown that important aspects of the chemistry of the steam reformer product can be duplicated using staged, small scale laboratory testing in sealed crucibles. [WSRC-TR-2003-00352, WSRC-MS-2004-00288, INEEL/EXT-03-01118]. The staged small scale testing was shown to be representative of pilot-scale testing and thus can be used to determine some aspects of process compatibility and initial conditions for larger scale testing [INEEL/EXT-03-01118].

Hanford evaluated Steam Reforming for use in the Initial Processing Module (IPM) in 1993 and 1994 [INEEL/EXT-04-01493]. It was not the technology of choice in part because the technology was not developed sufficiently. Since then, technology development includes a pilot plant (for non-radioactive materials) and a commercial nuclear waste treatment facility. Idaho has chosen Steam Reforming as the technology for the new facility being designed to process their sodium bearing waste (SBW) currently stored in tanks at that site.

Technical Overview

Figure 4-1 illustrates the proposed flow diagram for processing of Tank 48 TPB in the 241-96H facility and is used to describe the process. The figure is consistent with the Hazen pilot plant being used to test the flowsheet for the INL SBW. An approximately 3wt% TPB slurry is pumped from Tank 48 to the Feed System in the Steam Reforming Process. The Feed System concentrates the slurry to 10-20wt%. The concentration, not shown in the figure, probably can be achieved by cross-flow filtration. The concentrate is stored in a 50,000 to 100,000 gallon feed tank and then transferred to a feed batch vessel that continuously supplies concentrated waste to the Fluidized Bed Steam Reformer. It would also be possible to concentrate the waste just as it is fed to the process system; this option would still require a feed/surge tank to feed the process system.

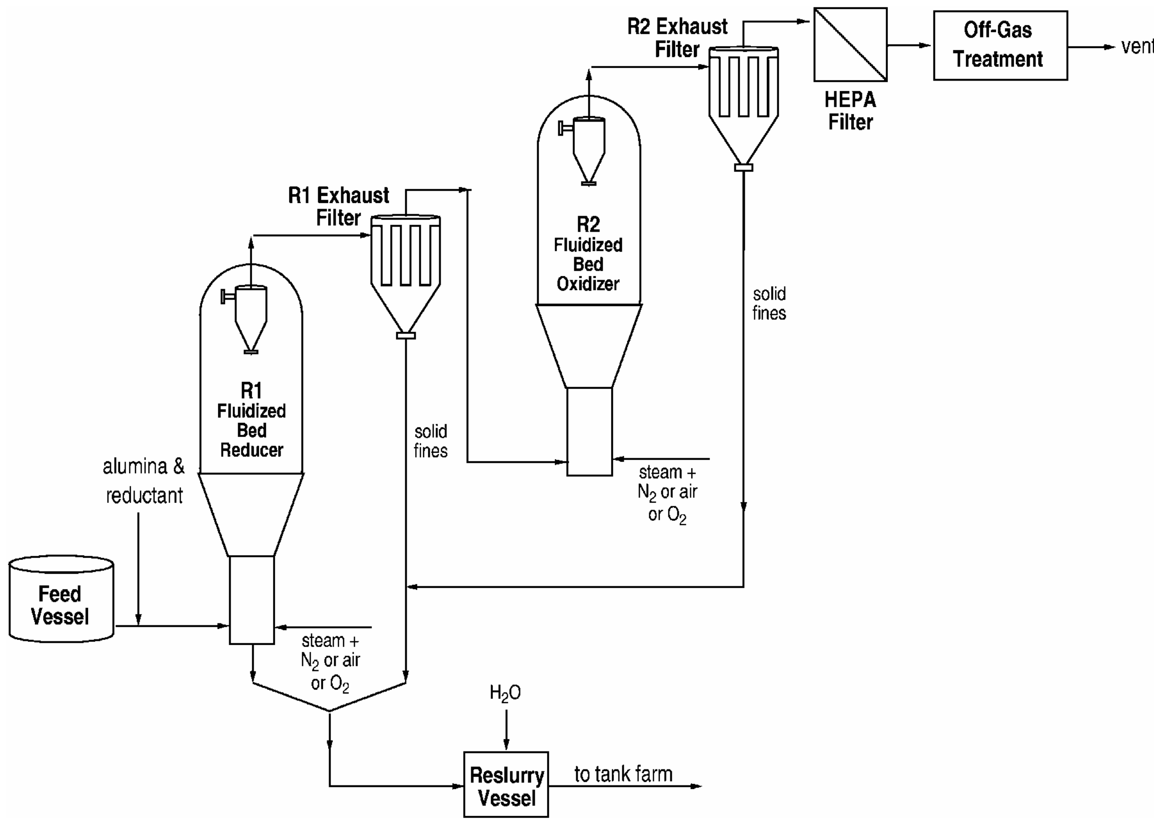


Figure 4-1: Steam Reforming Process

The steam reformer, about 22-inch in diameter, contains a bed of alumina (Al_2O_3) or Na_2CO_3 particles that are fluidized by superheated steam, a solid fuel (e.g., coal) and gaseous additives such as nitrogen, carbon dioxide, etc. The Steam Reformer is operated at 650-725°C where, within the Al_2O_3 or Na_2CO_3 fluidized bed, the TPB is pyrolyzed to benzene, simple hydrocarbons, and carbonates while the nitrates and nitrites are reduced to nitrogen. A cyclone separator is provided at the outlet of the Steam Reformer to recycle Na_2CO_3 fines that contain salts from the Tank 48 waste slurry. The Al_2O_3 or Na_2CO_3 bed particles are coated with Na_2CO_3 containing salts from the Tank 48 waste slurry and as they grow in size they fall out of the bed and are collected along with the contaminated Na_2CO_3 fines from the filter located in the off-gas. Solids exiting the reformer are slurried in water and sent to a waste tank. If alumina is used for bed particles they may be separated from the slurry, washed, and recycled to the fluid bed, although this may add unwarranted process complexity. If needed, fresh alumina is continuously fed with the waste stream to the fluidized bed to maintain its operation.

The filtered off-gas passes to a separate oxidizer where oxygen is added to a fluidized bed or a catalytic converter that converts the remainder of the organic compounds to CO_2 and H_2O. The off-gas will likely require further treatment to remove mercury and will be HEPA filtered prior to release to the stack.

Reactor Size

Evaluations were made of the potential for the Steam Reforming treatment for two cases to process Tank 48 waste at required capacities in the 241-96H facility (Appendix 4 for calculation details). These independent calculations were made to give the ITR Team assurance that reference information provided is defensible. The evaluations were based on information provided in the crucible bench scale tests [WSRC-TR-2003-00352] and the proof-of-concept test results obtained in the bench-scale 6-inch diameter fluidized bed system at the Science and Technology Applications Research (STAR) Center at Idaho Falls [INEEL/EXT-03-01118]. Our estimates predict that a steam reformer sized to process a concentrated Tank 48 waste stream (10wt% solids) in six months can fit in the 241-96H facility. The same steam reformer would require ~17 months to process the 250 Kgal supernate (3wt% solids).

The crucible tests defined conditions for the pilot scale tests of Al_2O_3 bed media to avoid sticking and particle agglomeration and recommend conditions of 650°C at 1 X stochiometric sugar, and 3-48 hrs solids residence time to make suitable Na_2CO_3 product for DWPF. In the STAR facility destruction of nitrate (>99%) was achieved, and TPB and derivatives were destroyed to <5ug/g. The pilot studies show that satisfactory Steam Reforming of Tank 48 simulant was accomplished in a bed seeded with alumina particles yielding feed products which adhere to the alumina particles causing particle growth but no agglomeration. Silica beds are an unsatisfactory replacement for the alumina beds because of agglomeration and defluidization.

No TPB or TPB decomposition products were detected on the solid products, and TPB destruction efficiency was greater than 99.98% based on detection limits. The bed product is largely Na_2CO_3, and benzene (with other hydrocarbons) is a residual in the off gas at ~85-94% conversion. The test was run in a reduction state and did not include oxidation required to convert the organic carbon to CO_2. A STAR-type gas phase oxidizer reactor sized for 99% benzene conversion may fit in the 241-96H facility as well (Appendix 4), but a second catalytic fluidized bed run as an oxidizer or a commercial catalytic oxidizer will be more effective and more compact than the vapor phase oxidation zone used in the STAR reactor configuration.

Downstream Processing

In addition to the reaction, the product fate must be considered. Clearly the Team must consider what happens to the Cs-137. Importantly, the Team must also consider what happens to the carbon.

The Cs-137, carbonates and potentially significant levels of residual fuel carbon are the primary components of the solid coming out of the fluidized bed and out of the filters. The solid samples observed from runs made for Idaho by Hazen also contained residual particles of coke. THOR and Hazen representatives advise that this carbon does not occur in processes run by adding sugar or polyethylene chips instead of carbon. However, there have not been tests with sugar or polyethylene; these tests need to be included in the proposed testing program. Demonstrating that an acceptable level of residual carbon in the solid product can be achieved at pilot-scale is a critical issue. The rest of the carbon is exhausted as carbon dioxide. Mercury present in the feed leaves the reactors as vapor, and may need to be removed from the gas stream prior to discharge. The ITR Team views downstream processing for Steam Reforming as achievable.

Visit to Hazen Research, Inc.

Four members of the ITR Team and Renee Spires and Richard Edwards of WSRC made a site visit to the Hazen Research Inc. pilot facilities in Golden Colorado on July 10, 2006 to evaluate their capabilities and seek answers to processing and design details. The personnel with whom the Team visited were representatives of THOR and Hazen Research, Inc. The visit included a tour of the pilot plant where the Team observed design details, and discussed operational experience, and process control capability. Details of past and recent tests performed on INL high SBW were presented. Mention was made of future tests to be performed with Tank 48 simulant.

Key findings from the Hazen site visit are:

- Results with monochlorobenzene studies demonstrated downstream processing capabilities to convert benzene and other hydrocarbons products from the reformer to CO_2 and H_2O. The possibility to eliminate alumina (Al_2O_3) as a starter bed with appropriately sized Na_2CO_3 particles was discussed and should be pursued. It is recognized that the latter particles are less dense and that an expanded bed will occur.

- The carbon addition as large charcoal particulates used in the INL, high SBW test lead to charcoal particles in the solid product. Such carbon is unacceptable in a DWPF feed due to carbon load and possible incidental metals in the charcoal. Other carbon sources such as sugars or, possibly, polyethylene should be used. These alternate carbon sources should be evaluated. Downstream processing of the off-gas should follow existing commercial practices employed in radionuclide operations for fines and volatile mercury removal; and

- The current INL design includes a second fluidized bed oxidation unit. An attractive alternative is the use of a commonly available catalytic oxidation unit to completely oxidize benzene and other hydrocarbons (e.g., CH_4) to CO_2 and H_2O.

Technical Issues and Risks

Based on calculations (Appendices 4, 5 & 6), and the references cited, the Team reached the following conclusions and observations regarding Steam Reforming.

Proof of Concept

Proof of concept has been demonstrated.

Fate of Carbon

- The potential for unacceptable levels of residual carbon in the solid product from Steam Reforming is a critical technical issue. Pilot studies should demonstrate the use of an acceptable fuel source and operating conditions to achieve production of a solid product that will meet feed criteria for DWPF.

- High levels of benzene and other hydrocarbons were in the product off-gas. Appropriate oxidizer reactor design will be required for acceptable destruction, or other means of treatment, such as catalytic oxidation, should be considered.

Kinetics and Reactor Residence Time

- The reducing bed geometry for Case 1 (i.e., 17-inches diameter and 17-feet high) provides the same solids residence as that used in the STAR facility. The pilot and crucible studies suggest that this is adequate contacting to achieve 99.98% destruction of KTPB to benzene. Pilot studies should confirm these results;

- The residence time to process the non-KTPB solids is much larger than the residence time needed to convert solid KTPB to volatiles. There are two characteristic residence times for the Steam Reforming; the first establishes the processing time to move non-TPB solids through the reducing bed and the second relates to the oxidization rate of volatiles released when TPB decomposes.

Design Concerns

- Equipment design can be minimized by using lessons learned from much of the Hazen design and from the INL design.

- Preliminary design studies need to confirm that the Steam Reforming process, scaled to process at the necessary feed rate, can fit within the available space in the 241- 96H facility.

- A pilot plant (Hazen) exists which has a footprint consistent with the available space in the 241-96H facility. 'Cold' pilot plant runs are to be made on the Tank 48 slurry simulant in the next few months.

Issues for Steam Reforming

Although the Steam Reforming process has many positive attributes, there are a number of issues that need to be addressed before implementation is confirmed to be feasible. It is expected that these issues can be addressed in bench and pilot scale test programs prior to the final design and construction phase. Issues and information necessary for resolution follow.

Fate of Carbon

- Acceptable elemental and/or organic carbon in product to DWPF: It should be demonstrated in defining pilot studies that the solids product has acceptable forms and levels of carbon;

- Acceptable fuel/reducing agent: The form of carbon to be employed as a fuel/reducing agent (e.g. carbon, polyethylene, sugar, etc) is an important issue. Use of large carbon particles leads to unreacted carbon particles in the Na_2CO_3 product. Studies are necessary to determine a suitable reductant;

- Benzene and hydrocarbons in off-gas: Determine benzene and hydrocarbon levels from reducing bed under desirable operation ranges and method of disposition. For destruction of benzene and other carbon compounds, the oxidizer reactor or catalytic oxidizer operation conditions need to be defined, and the ensuing reactor geometry should be compatible with space requirements in the 241-96H facility. Acceptable destruction should be demonstrated in pilot studies. Should venting the benzene be an acceptable alternative appropriate permitting should be pursued.

Kinetics and Reactor Residence Time

- Acceptable level of KTPB destruction: Range of solids residence time, T and P for acceptable destruction of KTPB for 3wt% and 10wt% solids in supernate should be determined in pilot studies. The 20-hour residence time related to the bed dynamics appears to be excessive, and shorter residence times should be studied;

Design Concerns

- Solids handling issues: 1) it should be demonstrated that fines do not escape the primary off-gas filtration system. 2) it is anticipated that solid bed products will not be transported to DWPF. Accordingly, conditions should be determined and demonstrated for producing a suitable slurry for transfer to the tank farm. 3) should solids coat Steam Reforming equipment, the design should provide for equipment decontamination;

- Agglomeration and defluidization: Operation ranges for flow rates of slurry feed, carbon source, alumina, O_2, fluidizing steam, and atomizing air that will avoid agglomeration and defluidization must be determined;

- Demonstrate acceptable level of mercury in the off gas: An appropriate mercury removal system may be required; and

- Perform a preliminary design to ensure that all of the necessary equipment can fit within the 241-96H facility.

Resolution of these issues would minimize risks in the implementation of Steam Reforming processing technology for successful treatment of Tank 48 slurry.

ITR Conclusions Regarding Steam Reforming

In the Team's opinion, Steam Reforming is likely to be a technically feasible processing concept, and it is likely that it can be made to fit within the 241-96H facility. As more detailed kinetic data become available, a better estimate for the size of an integrated reduction/oxidation reformer will be possible and the size required will be smaller than the conservative estimate obtained in Appendix 4. A preliminary design study will confirm if the equipment can fit into the 241-96H facility.

4.3 Wet-Air Oxidation

WAO has been recognized for many years to be a useful method for destroying toxic organic compounds. The original patent appeared in the early part of the 20^{th} century, and significant applications began as early as the 1930s. In most cases, the destruction rates appear to be high, so a relatively small facility can treat wastes rapidly. Because WAO studies made up to 1991 are reviewed by Li, et al., [PIT-MISC-0173] the ITR has focused on studies made since then.

Although WAO is a mature technology for non-radioactive situations, but there are no known applications of WAO involving significant radioactivity, and there are no published data on destruction of TPB.

WAO was considered in 1994 for destruction of organic compounds and ferrocyanide in tank waste at Hanford. An extensive study was conducted of several process options, and WAO was selected as the most attractive option. Although none of the options was implemented, the studies did advance to an early conceptual design stage [PNL-SA-23181].

Thus, the potential use of WAO oxidation to destroy TPB must be evaluated based upon experience at non-nuclear applications and a limited amount of data on destruction of compounds like TPB. SRS is planning tests of TPB destruction at the laboratories of a commercial vendor of WAO technology, and the results from those tests should make possible much better assessment of the applicability of WAO to Tank 48 waste; in particular, the tests will show if WAO can reduce the soluble organic carbon to sufficiently low levels in practical size equipment.

Technical Overview

WAO of TPB is assumed to follow the general path shown in Figure 4-2. The TPB is believed to breakdown quickly at 300°C to release benzene and a portion of the TPB may be transformed to soluble organic compounds such as phenol and/or acetate. These compounds are degraded to/toward CO_2 and H_2O. The literature data can be helpful in understanding degradation of these remaining soluble organic compounds, and there are more data on phenol than on other compounds.

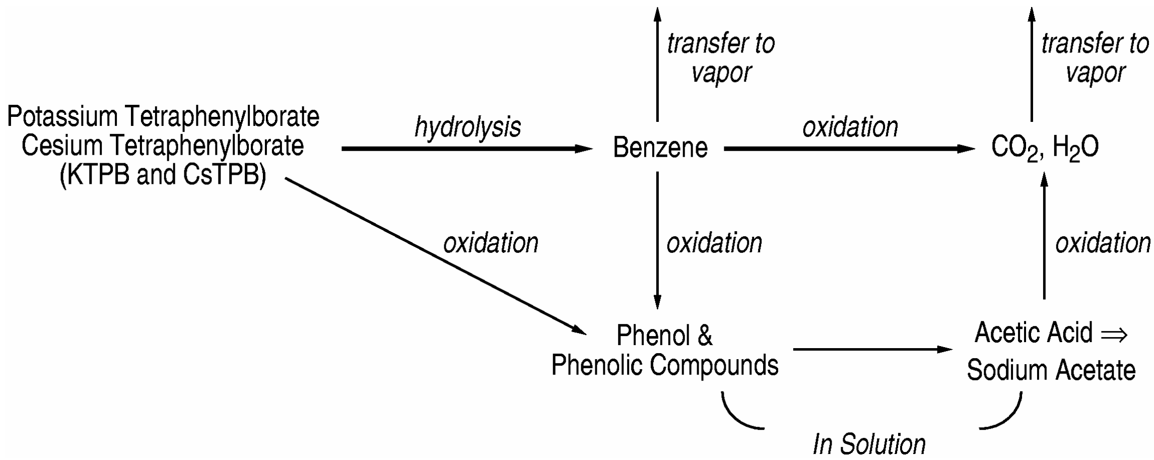
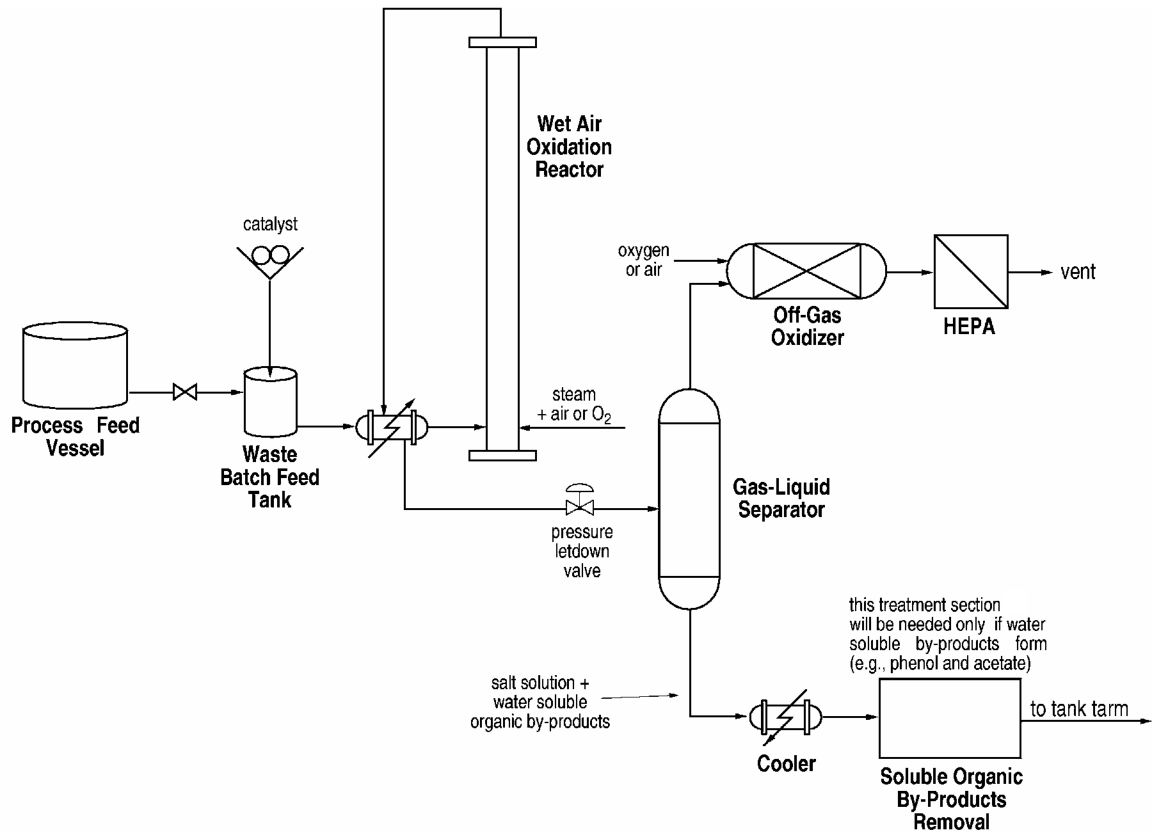


Figure 4-2: Wet-Air Oxidation Chemistry and Routes to Vapor-Borne and Water-Borne By-Products

A simplified flowsheet for WAO is shown in Figure 4-3. If feed from Tank 48 can be filtered to increase the concentration of solids (mostly TPB) from approximately 3wt% to 10wt%, the volume of waste to be processed can be reduced by a factor of approximately 3. That would reduce the size of a treatment facility required to treat all of the waste in Tank 48 by the same factor.

The reactor itself is shown as a vertical tower operating as a tubular reactor, but other reactor shapes have been used. Typical WAO reactors are bubble columns with baffles to reduce axial mixing of the liquid and redistributors to keep the gas bubbles of moderate size and well distributed in the reactor cross section. The reactor operates at a moderately high temperature, between 200 and 300°C and at high pressures, near 100 atm, or higher. The reactor can operate with or without a liquid or solid catalyst. While high pressures are commonly used in waste treatment facilities, the high pressure will make safe design and approval more difficult for high-activity applications. This is an issue identified in the Hanford IPM down-select document. Since WAO often does not convert all of the carbon in organic compounds completely to CO_2, many WAO applications with (non-radioactive wastes) toxic compounds produce non-toxic products that can be released or destroyed in bioreactors.



Note: The formation of water soluble by-products is common in WAO processes. For TPB destruction, the potential for the formation of phenol and acetic acid (converted to sodium acetate at high pH) must be considered.

Figure 4-3: Wet-Air Oxidation and Downstream Treatment Options

For the Tank 48 case, the fate of the organic compounds remaining after WAO must be evaluated carefully. WAO systems have been built with double columns to enhance destruction of troublesome compounds. If a significant fraction of the organic carbon still remains, the treated product may not be suitable for DWPF or for returning to the tank farm. If the degradation products from TPB produced by WAO can be processed through the SWPF, it was suggested that little or no additional downstream processing may be needed, but this option is not considered a likely choice since SWPF may not be available as Tank 48 waste is being processed and SWPF operating time may be solely needed for treating salt waste, its primary mission.

As noted, while the ITR evaluation was being made, a contract was being prepared for an industrial firm (Zimpro) to test WAO using a Tank 48 simulant. Important additional data should become available in a few months.

In the meantime, the ITR Team looked at available data on WAO of soluble compounds like those that could be formed from TPB. Phenol is the most relevant. During WAO, a substantial portion of phenol appears to be oxidized to CO_2 and H_2O, but still a significant fraction appears to be degraded only to intermediate compounds. The portion of phenol that is oxidized directly to CO_2 and water varies with different conditions and with different investigators. The subsequent degradation of the intermediate compounds can be very slow. Although a variety of compounds may be formed, acetate appears to be the major one, and its degradation rate is particularly slow. One study using a homogeneous copper catalyst showed good degradation of phenol, but did not confirm complete degradation to carbon dioxide or carbonate [PIT-MISC-0175].

Studies have indicated that the TOC can be reduced by WAO, implying that at least a portion of the carbon in phenol is being oxidized to CO_2. None of the studies has shown the TOC to be reduced to zero. Zhang and Chuang [PIT-MISC-0179] showed that TOC reduction increased significantly with increasing reactor temperature. Using as supported Pd-Pt catalyst, they showed as much as 80% reduction in TOC at 443K. The TOC level at which degradation ceased also increased with the amount of catalyst used in the reactor. These data suggest that the activation energy for oxidation of phenol directly to carbon dioxide is greater than that for oxidation to acetate (or other intermediate compounds) and that the catalyst is more effective in promoting oxidation of phenol to carbon dioxide. These results contradict an earlier study by Ploos, van Amstel, and Rietema [PIT-MISC-0178] which showed up to 90% TOC destruction without much effect of temperature. Baillod, et al., [PIT-MISC-0180] reported that higher temperatures affect the rate at which the TOC approaches its final or asymptotic value, but not the magnitude of this final asymptotic value. Their data suggest that temperature does not affect the fraction of phenol that goes directly to carbon dioxide. Discussions with the Zimpro staff[9] indicate that acetate can be oxidized to CO_2, but higher temperatures (and pressures) are needed. Thus, it is important to determine what quantities of acetate will be formed in WAO of TPB. The amount of soluble organics, and acetate particularly, will be determined in the tests SRS is planning at Zimpro. Zimpro, in very preliminary exploratory tests at non-optimized conditions, showed no detectable acetate in the liquid product; this was a promising result.

Reactor Size

Without sufficient data for even a conceptual sizing of a WAO unit, only approximate size of potential WAO reactors can be estimated. Reactor size requires specifying a flow rate and a reaction time. If the waste in Tank 48 is concentrated to 10wt% solids, a 0.35 gal/min flow rate could treat the waste in approximately one year of processing with the expected plant availability. Even allowing for anticipated reactor down time, this is a reasonable processing rate.

[9] Personal communications with Zimpro staff at Rothchild, WI, July 10, 2006.

Estimating a reaction time is more speculative. Zimpro experience suggests that a liquid residence time of approximately 1-hour and a gas residence time of about 10 minutes would be reasonable for WAO of TPB. These are only estimates from experience; they are not based upon test data. In a few months, the planned SRS sponsored tests at Zimpro will address the question of required residence time (and, thus, reactor size). These suggested residence times would require a reactor with a little more than 20 gallon volume, to process the contents of Tank 48 in approximately one year of processing with the expected plant availability of 50% and after the waste has been concentrated to 10wt%. That would not be an unreasonable size for the reactor, and it probably would fit in the 241-96H facility, along with the necessary support equipment. However, note that the support equipment required for WAO have not been designed and was discussed only qualitatively by the ITR Team. The height of the WAO reactor also could be a factor in fitting a WAO unit into the 241-96H facility. The typical height for WAO reactors is approximately 25-feet (Zimpro discussions, July 10, 2006). This height is reasonable and probably within the height available in the 241-96H facility, but the reactor could be made somewhat shorter if necessary.

Chemical additions for WAO that could affect DWPF would consist of any soluble catalyst added, and Fe is the additive that has been most studied. There is already significant Fe in the waste, and a sufficient amount may already be in solution to catalyze the oxidation. If breakdown of TPB is more difficult than expected, a Cu catalyst may be helpful. These components should not significantly affect DWPF glass volume. WAO could affect the nitrate/nitrite balance and require some change in the redox adjustment of DWPF feed, but that doesn't appear to be a serious problem.

Although concentration of the feed by filtration was desired to keep the reactors for all process options, the ITR also considered the use of feed directly from Tank 48 without concentration by filtration. If concentration of the feed from Tank 48 is not desired or acceptable, the reactor volume would be approximately three times larger, or the processing time would be approximately three times longer. This would be a significant increase, but the reactor should still be small enough to fit into the 241-96H facility. The increase probably would come largely in the diameter of the reactor, but even slight increases in operating temperature (and pressure) would be another option to triple the reaction rates.

Downstream Processing

WAO is expected to produce benzene and CO_2 (mostly as Na_2CO_3) as indicated in preliminary tests at Zimpro, but other organic compounds could be formed. Ideally, only CO_2 (or Na_2CO_3) would be produced. Then the slurry produced can be directly sent to DWPF. Alternatively, only benzene could be produced. Because it boils out at 80° C and is only sparingly soluble in water; this can be easily stripped as detailed below. The remaining slurry can then be sent to DWPF.

The Team found little data on what organic compounds are in fact produced by WAO of TBP. The Team suspects that the products could include compounds other than benzene and CO_2. While exploratory tests at Zimpro did not find phenol or acetate, definitive tests are needed and are planned. If phenol and acetate are produced in quantities that are above limits imposed by DWPF processing, WAO would look less attractive.

Possible treatment technologies for these organic compounds are listed in Table 4-1. All are feasible. Because benzene boils at 80°C, it will evaporate under most reaction conditions, and any dissolved benzene that remains can be easily stripped with nitrogen. The Team estimates stripping 90% of this dissolved benzene will take 10 minutes; 99% will take 20 minutes. Catalytic oxidation of the resulting benzene vapor has been carefully considered at SRS, especially using propane as a supplemental fuel [WRSC-RP-93-1184; RTE-ITP-96-267]. Adsorption on carbon is a second possibility, though this generates a secondary waste stream [SRT-LWP-94-147].

Reaction Product	Treatment
Benzene	Evaporation or air stripping plus catalytic oxidation
Phenol	Extraction; possibly will require further oxidation
Acetate[(a)]	Extraction, possibly
Carbonates[(b)]	None: compatible with glass
Carbon Dioxide	None

(a) Including acetic acid, sodium acetate, etc.
(b) Including sodium carbonate, potassium bicarbonate, etc.

Table 4-1: Possible Further Treatments for Carbon-Containing Reaction Products

In contrast, separation of phenol seems less well developed. Phenol has a boiling point of 182°C and a 7% solubility in water at a pH below the pK_a of 9.9. Two separations seem possible for phenol. First, if the pH is lowered to below the pK_a, the phenol could be extracted into an organic solvent. The disposal of this stream has not been considered. Second, at the current high pH, the cesium can be extracted using the solvent in the new SWPF, but the SWPF is not expected to be available until Tank 48 is available, and it is not likely to be desirable to divert a significant part of the SWPF operating time from its primary mission of processing salt waste. The resulting, phenol-containing raffinate could then be sent to Saltstone. In a note[10] to

[10] Personal Communication from D.T. Conrad, July 3, 2006.

David Kosson (7/3/06), D.T. Conrad (WSRC) says that in Saltstone, “phenols are not restricted.” [LWO-LWE-2006-00022] However, it is suspected this may be because the potential amount involved has not been carefully evaluated.

The separation of acetate has similar problems to the separation of phenol. At a pH below the pK_a of 4.75, acetate will be converted to acetic acid, which has a boiling point of 118°C and is difficult to strip. (This is a major unrecovered waste stream in the American chemical business.) The obvious alternative is the same for phenol: extract the cesium from the mixture of reaction products using the Caustic Side Solvent Extraction process to be installed in the SWPF, and send the acetate-containing raffinate to Saltstone. Acetate restrictions on Saltstone are unclear, but can potentially be overcome by blending. However, as noted earlier, the availability of SWPF and the compatibility of significant acetate with the solvent in SWPF are questionable, and the Team does not recommend counting on use of this option.

Unlike Steam Reforming, WAO will probably not require mercury vapor capture. The mercury will stay in ionic form, and be carried forward with the liquid.

The Team does not know the detailed composition of the streams produced by the proposed decompositions, this section points out that any decomposition method that removes organic carbon as carbonate or as CO_2 gas has a major advantage.

Zimpro Visit

Two members of the ITR Team and Kofi Adu-Wusu of WSRC visited the Zimpro facilities at Rothschild, WI, on July 10, 2006, to discuss the applications of WAO to the Tank 48 problem. Zimpro is a part of U.S. Filter that is now owned by Siemens, a large German company (and “U.S. Filter” will change its name to “Siemens” in the near future). Zimpro is the largest supplier of WAO technology in the world and has almost all of the U.S. market. The ITR visitors were impressed with the technical expertise of the Zimpro staff and the capability of their facilities. For a moderately small company, their analytical chemistry, laboratory testing, pilot testing, and manufacturing capabilities were impressive.

SRS plans to contract Zimpro to test the removal of TPB and its soluble degradation products by WAO. These tests will probably be completed in the fall of 2006.

The visit included a discussion of tasks that could be included in that contract. The visiting Team stressed that the goal is the destruction or removal of TPB without leaving soluble organic carbon in the solution. Destruction of TPB (alone) is not a sufficient goal. Additional processes to extract organic carbon may be possible, but not desirable. The potential advantages of concentrating the Tank 48 wastes to 10wt% solids by filtration prior to processing were also discussed.

Zimpro shared some results from very exploratory measurements. Using relatively non-aggressive conditions, they were able to decompose or destroy a large fraction of the TPB, and with the use of a higher temperature and pressure and a soluble catalyst (probably a few hundred ppm of Cu ions), they should be able to raise the fraction of TPB destroyed close to 100%.

Most importantly, these very preliminary data showed no detectable presence of soluble organic compounds. Approximately half of the carbon in TPB was converted to dissolved inorganic carbon (carbonate) and the remaining carbon was in volatile hydrocarbon, probably benzene. Although those results were very preliminary, they were viewed as encouraging.

Technical Issues and Risks

Based on its review and evaluation, the ITR Team reached the following conclusions and observations regarding WAO.

Proof of Concept

WAO is a mature technology for several non-radioactive applications; there is considerable experience with the technology.

Fate of Carbon

- Few data are available for breakdown of TPB in WAO that can predict the reaction products or reaction rates; only two exploratory tests have been made on TPB. Very preliminary testing of TPB destruction indicates significant destruction and limited residual acetate.

- If significant concentrations of soluble intermediate organic compounds are formed that are difficult to destroy by WAO, such as phenol or acetate, it will be more difficult to approach sufficient removal of the TOC to meet DWPF requirements and WAO would be considerably less attractive. Discussions with Zimpro indicate that high destruction of even acetate, probably the most stable compound likely to be formed, is possible but requires higher temperatures, and, perhaps, higher catalyst concentrations.

- WAO is likely to require an off-gas system that can handle benzene that may be equivalent to a significant fraction of the benzene in the original TPB. This transfer of benzene quickly to the gas phase is not viewed negatively since quick removal of benzene via the off-gas probably minimizes the formation of soluble organics that could be difficult to oxidize.

- While there are no data on the effect of high nitrate/nitrite concentrations on WAO, the nitrate could help with the WAO destruction processes.

Kinetics and Reactor Residence Time

The reactors are relatively compact, largely because most of the reactor is filled with the liquid slurry.

Design Concerns

- No additional solids are added to the system, and solids handling is not expected to be a significant issue.

- The high pressures required impose safety considerations that are not routine for the site. These issues could increase the time for approval. However, one should note that WAO reactors are filled largely with liquid, not gas. Only about 15% of the reactor, volume is filled with gas. The pressure energy released from a failure in a liquid filled reactor is less than that from a gas filled reactor.

Issues for WAO

Although WAO offers promise, several issues would have to be resolved before it could be used for Tank 48 waste:

- There is no experience in using WAO with highly radioactive waste. Although WAO oxidation is a mature technology, this lack of experience would require more design efforts for remote operations and maintenance.

- There are only preliminary data on destruction of TPB. This issue will be addressed during a planned contract from SRS to Zimpro. The brief tests planned should show whether TPB can be destroyed effectively and what degradation products are formed.

- Although it appears that a WAO system could fit into the 241-96H facility, that information would need to be confirmed by a preliminary design.

ITR Conclusions Regarding WAO

WAO is considered a promising process option, but these issues will have to be resolved. WAO very likely could be made to work. The lack of experience with design and operation of WAO in similar applications with high levels of radioactivity, the very limited data on destruction of TPB by WAO, and the safety concerns associated with high pressures, even liquid pressures, are the key issues with WAO.

4.4 Fenton's Reagent

Although Fenton's Reagent is not one of the processing technologies currently included in the WSRC path forward, it has considerable potential and continues to interest DOE. The Fenton's Reagent process was first discovered more than 100 years ago and has become a well established technology for destroying organic compounds. It is a common option for cleaning up contaminated soils.

Technical Overview

The basic chemistry of the Fenton's Reagent reaction is quite similar to that employed in WAO with highly oxidizing hydroxyl radicals produced from hydrogen peroxide instead of being produced thermally. Ferrous iron in Fenton's Reagent acts as a true catalyst and is cycled between +2 and +3 oxidation states during the process. The reaction is carried out between room temperature and 100°C and is most effective at pH values between 3 and 5. In this pH range, the peroxide and hydroxyl radicals have longer lifetimes and oxidation reactions compete more effectively with peroxide decomposition to O_2 and H_2O. At higher pH, the oxidation reactions still occur, but faster peroxide decomposition limits the production rate of hydroxyl radicals and the oxidation chemistry is significantly less effective. The amount of peroxide required can be considerably more than the stoichiometric amount needed to oxidize the organic material because of the decomposition side-reaction:

$$K\left[B(C_6H_5)_4\right] + 60H_2O_2 \longrightarrow KBO_2 + 24CO_2 + 70H_2O$$

In addition, the nitrites in Tank 48, which are present at moderately high concentrations, will be oxidized to nitrates resulting in yet higher peroxide consumption.

Fenton's Reagent reactions are usually carried out in batch reactors, and for Tank 48 waste, the reactions could be in the original tank (Tank 48) or in a separate and smaller tank. To use Fenton's Reagent reactions in Tank 48, the pH would have to be maintained at least as high as 11 to avoid intolerable corrosion. Under these conditions, rates are slow, with only 13% TPB decomposed after ~75 days [WSRC-TR-2004-00306, p21].

Out-of-tank use of Fenton's Reagent is a more acceptable possibility from the standpoint of corrosion. An out-of-tank reactor made of stainless steel allows operation at lower pH and at higher temperatures, both of which accelerate the reaction rate. Batch operations necessarily increase the size of the reactor needed relative to continuous operations. A significant amount of time is required to charge the KTPB slurry to the reactor, add nitric acid to lower the pH, heat the reactor contents, meter in peroxide to maintain an optimal Fe^{2+}/H_2O_2 ratio during the reaction, destroy the excess H_2O_2, add sodium hydroxide to make the solution highly caustic again, cool the reactor contents, and discharge the vessel. Some parts of this sequence can be done in parallel, but generally, the multi-step operation is time-consuming and this limits the productivity of the reactor.

Unlike a continuous reactor (e.g., WAO), batch operation allows water-soluble by-products (phenols, acetates) to be held in the reaction zone for the time needed to completely oxidize them to CO_2 and H_2O. Data for Fenton's Reagent reactions on KTPB [ORNL/TM-2003/262, WSRC-RP-2004-00240] indicate that the copper-catalyzed, acidic conditions employed are especially effective at hydrolyzing TPB resulting in a rapid release of benzene early in the reaction sequence. At high temperatures especially, the low solubility and high volatility of benzene lead to nearly instantaneous separation of the compound to the vapor phase in the top of the reactor. As also noted by Taylor [ORNL/TM-2003/262], the Team is quite sure that the low TOC levels measured in these tests result, in significant part, from the rapid venting of benzene away from the aqueous phase.

In principle, it would also be possible to carry out the operation in two steps. First, the pH would be lowered, catalyst would be added, and the temperature would be increased to approach the boiling point. This may allow most of the TPB to be hydrolyzed to release its benzene. Then the benzene could be flushed out of the reactor under a nitrogen blanket. Once the benzene is removed, the peroxide could be added to destroy any remaining organic compounds. Once peroxide is being introduced to the reactor, it will not be possible to maintain an inert blanket to prevent ignition of benzene in the headspace or elsewhere in the off-gas system. In this two-step mode, the operation could be viewed more as a hydrolysis reactor and less as a Fenton's Reagent reactor. This two-step operation would increase the overall batch reaction time and would, in turn, increase the size of reactor vessel needed.

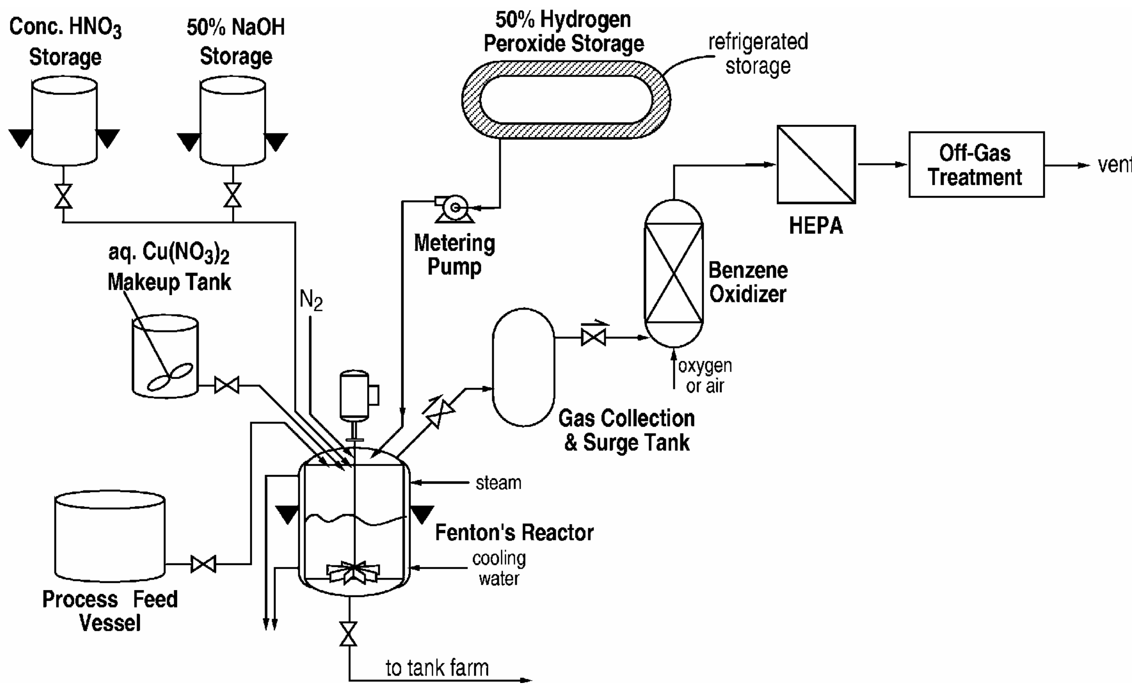


Figure 4-4: Process Flow Diagram for Fenton's Reagent on Tank 48 Waste

Fenton's Reagent has been used in numerous applications, included the destruction of radioactive ion exchange resins at Oak Ridge [ORNL/TM-2002/197]. More significantly, tests have been made with TPB and simulants of the waste in Tank 48. Although the simulants used appear to include some errors in the amount of MST used, the results may still be meaningful. With more MST, foaming may be more serious, but there is no apparent reason to expect the degree of TOC removal from the liquid phase to be affected significantly. A proposed flowsheet for Tank 48 processing is showing in Figure 4-4.

Fenton's Reagent oxidation technology is being marketed by AEA Technologies. Wilkes and Mitchell [WSRC-RP-2004-00240] carried out laboratory-scale out-of-tank reactions using a low MST simulant, and these tests were confirmed independently at Oak Ridge National Laboratory (ORNL) [ORNL/TM-2003/262] using simulants and conditions suggested by AEA Technologies. The approach involved two steps. The waste was heated and neutralized to a pH of 7.5 before peroxide was introduced. The final temperature of the reaction was not given but probably approached the boiling point. At the lower pH, much of the TPB hydrolyzed to benzene and oxidized to soluble products. Some of the benzene that formed was captured by a reflux condenser, returned to the liquid phase reaction zone, and oxidized by the peroxide. However, it is believed that a significant fraction of the benzene was removed to the vapor and vented. In the ORNL study, about 50% of the potentially available benzene was removed to the vapor. A surge of gas emissions was noted as the temperature reached the 50 - 70C range. This surge might have been CO_2 released from Na_2CO_3 in the simulant by the acid that was added, or the surge could have been benzene vapor, or it could have been a combination of the two. In any event, the ORNL data indicate an early and substantial release of benzene under essentially identical conditions to those used by AEA Technologies. After reacting for approximately 1-hour, the pH was lowered further to 3.5, and the reaction continued for several hours by metering peroxide into the reactor. The pH was maintained near the optimal value by periodic additions of sodium hydroxide.

Both studies indicate that more than 95% of the TOC can be removed using Fenton's Reagent. The ORNL study actually showed more than 99.9% removal using the reference conditions and better than 99% removal in all tests except one with a "washed" simulant. The SRS work gave a 98% destruction, without a product analysis [WSRC-RP-2004-00240]. In the AEA tests, the off-gas was not analyzed for benzene, but, as noted earlier, the ORNL tests found that as much as 50% of the TOC was evolved as benzene early in the tests, perhaps even during the heat-up when the AEA report suggests strong off-gas emissions. Again, a substantial fraction of the TPB apparently hydrolyzes very quickly to benzene which is easily vaporized at the elevated temperature. The remaining TOC was then largely oxidized by the Fenton's Reagent.

In the AEA flowsheet, probably typical of those likely to be used for Tank 48 waste, the final waste after TPB destruction has a volume that is approximately twice the original waste volume. This increase in volume results from acid added to lower the pH, sodium hydroxide added to control the pH, and water added with the peroxide. The tests at AEA and ORNL used approximately 50% peroxide solutions. This increased waste volume could be reduced by evaporation, but the added sodium would still require treatment. When the required amount of NaOH is combined with the HNO_3 needed to acidify the waste prior to reaction, 8.5 Kg of $NaNO_3$ are generated for each Kg of KTPB or CsTPB processed. The additional $NaNO_3$ increases the total soluble solids in the reactor effluent from about 18wt% to about 28wt%. Additional water and NaOH may be needed to adjust the total solids and maintain the high pH before returning the effluent to the tank farm. In all these tests, there was some concern with accumulation of deposits on the reactor walls. Some solids were seen on the glass reactor used at ORNL; the concern would be with accumulation of solids after numerous reaction cycles. It is important that these not be polycyclic aromatics, tars, or other similar organic compounds.

Because of initial concerns that TPB destruction with Fenton's Reagent could be incomplete, the ITR Team also considered using other, stronger oxidizing agents. One obvious alternative is potassium permanganate, which is an even stronger oxidizer than is Fenton's Reagent. $KMnO_4$ solution also quickly degrades the TPB and is believed to degrade the by-products produced. Several of us know from our own experience that the kinetics are fast; however, the reaction stoichiometry makes clear the impracticality of using permanganate as an oxidant for the TPB.

$$K\left[B(C_6H_5)_4\right] + 40KMnO_4 + 10H_2O \longrightarrow KBO_2 + 40MnO_2 + 24CO_2 + 40KOH$$

Reacting one mole of TPB requires 40 moles of potassium permanganate. In terms of mass, reacting 1 Kg $KB(C_6H_5)_4$ produces 9.7 Kg of MnO_2. The MnO_2 dramatically increases the mass of solids subsequently to be processed. The Team estimated that DWPF would have to be dedicated for 4.5 years to processing only the waste from Tank 48 if the TPB in the tank were oxidized using only $KMnO_4$. The use of $KMnO_4$ does not merit further consideration.

Reactor Size

Although the reaction rates for Fenton's Reagent can be high at optimal pH and high temperature, large reactors are required. ORNL tests of 4-hours showed better than 99% TOC removal, but considerably more time is required to allow for filling, neutralizing, heating, and discharging the reactor contents. AEA suggested that a batch cycle time of approximately 12-hours is needed, and this appears reasonable with a reaction time of 4-hours.

If the contents of Tank 48 can be filtered to concentrate the solids to approximately 10wt%, a processing rate of approximately 0.35 gpm would treat all of the wastes in Tank 48 in less than 170 operating days. If the waste were not filtered, the operating time or the processing rate would have to be increased by approximately a factor of three. Because there are no data on operating with 10wt% solids, additional tests are needed to show that Fenton's Reagent is effective with a higher solids loading. A higher solids level will increase foaming due to the high Na_2CO_3 content, and a higher peroxide addition rate will be needed to keep the percent removal rate as high as observed at a lower concentration. The total soluble solids increase after reaction will be lower, but residual benzene and/or soluble TPB in the filtrate must be dealt with.

Using the processing rate of 0.35 gpm and a 12-hour batch reaction cycle, approximately 250 gallon waste volume would be in the reactor. If the treatment doubles the volume as reported by AEA, the volume of liquid needed in the reactor would be approximately 500 gallons. Since considerable foaming was reported in laboratory tests, considerable freeboard will be needed in the reactors. It may be reasonable to allow a 100% freeboard leaving a reactor volume of approximately 1,000 gallons. The reactor volume could be in a single reactor or in two or more smaller reactors. However, the use of multiple reactors with multiple valve, heating/cooling, and control systems will add to the equipment costs.

One problem that is common to all options for processing the wastes from Tank 48 is a suitable off-gas control system. However, a Fenton's Reagent reactor imposes a more difficult off-gas control design because benzene is likely to be released in large quantities over a short time. Laboratory tests at ORNL indicated that approximately 50% of the carbon is released as benzene gas early in the reaction. Thus the off-gas system for a Fenton's Reagent reactor would have to remove benzene and eliminate the potential for benzene accumulation. If the Fenton's Reagent is introduced immediately, there is a danger that benzene will be evolving while oxygen is also being released from the tank from breakdown of peroxide. This situation is clearly undesirable. As noted earlier, it may be possible to add a preliminary step to hydrolyze the TPB before peroxide is introduced, but the extra step would increase the batch reactor cycle time and, thus, require a larger reactor to maintain the same processing rate.

The ORNL tests also showed solids accumulation that blocked a small diameter reflux condenser. The problems was solved by using a larger diameter condenser, but the experience shows that solids can also be entrained into the off-gas and would have to be handled in the off-gas treatment.

Downstream Processing

Fenton's Reagent produces a slurry which can in principle be fed to DWPF for vitrification. However, to carry out the reaction, acidification with nitric acid is required. Thus, the mass of solids in the glass produced is more than trebled. If the slurry must be made basic again for storage, then the mass of glass produced rises still more: about 8 Kg additional glass for every Kg of KTPB treated.

The slurry produced with Fenton's Reagent may contain a variety of organic compounds. The data from initial Fenton Reagent tests do not show residual soluble organics, and that is encouraging. If the only compound produced is benzene, slurry treatment will center on benzene stripping. If the reaction time is sufficiently long, then the chief product could be carbon dioxide. If compounds like phenol and acetate are produced in significant quantities, then the treatment of the slurry is more complicated.

Technical Issues and Risks

Although Fenton's Reagent has been shown to be capable of destroying (or volatizing) large fractions of the carbon in TPB and probably could be used to treat the wastes in Tank 48, several issues will be important in considering the use of Fenton's Reagent.

- The use of large quantities of hydrogen peroxide will cause important safety issues. Although Fenton's Reagent has been used at least once with radioactive materials [ORNL/TM-2002/197], the level of radioactivity was much lower, and the scale of the operations was much smaller. The use of hydrogen peroxide in large quantities will introduce a new hazardous material to the SRS.

- The sudden release of benzene early in each batch treatment will require careful safety review. The size of a single reactor and the potential for large fractions of the benzene content of a TPB batch reaching the reactor headspace will raise serious safety concerns. Additionally, there is the potential that peroxide decomposition will increase the O_2 concentration in the reactor headspace thereby increasing the risk of explosion in a sizable vapor phase.

- The off-gas system will have to be designed to avoid accumulation of large quantities of benzene anywhere in the piping system where it can ignite. While this is a potential problem for all processing options for Tank 48 wastes, the sudden release of the benzene over a short period makes the hazard more serious in the use of Fenton's Reagent.

- The large reactor volume needed could be a problem for fitting into existing space at the 241-96H facility and for remote maintenance. The reactor itself would be difficult to replace and large vessels can make it more difficult to reach other equipment remotely. The 1,000 gallon reactor size estimated above is considered to be about as small as one could expect. If the feed is not concentrated to approximately 10% solids as assumed in this estimate, the reactor volume would have to be approximately 3,000 gallons. Adding caustic to the acidified waste to return it to pH 14 for storage in any of the existing SRS tanks prior to treatment in DWPF could increase the batch cycle time further. If it should be necessary to run the reactor in two steps to avoid benzene release while adding peroxide, the cycle time could be increase further. Each increase in the cycle time increases the size reactor required and increases the difficulty of placing the reactor volume in the 241-96H facility. A preliminary design of a complete facility using Fenton's Reagent will be necessary to insure that all of the equipment can fit within the 241-96H facility.

- The longer the reactor cycle time, the larger the inventory of reactivity in the reactor for a given overall Tank 48 processing time. The ITR Team focused upon the volume of the reactor and the difficulty in fitting it, along with associated equipment, into the 241-96H facility, but the Team was informed late in the study that the safety requirement for the 241-96H facility would limit the amount of radioactivity that could be in the 241-96H facility at any time. The large volume of the Fenton's Reagent reactor, even the 1,000 gallon reactor discussed above would contain much of the radioactivity allowed and leave little room for radioactivity in other equipment. Significantly increasing the reactor cycle time would make the problem worse. The amount of radioactivity in the batch reactor depends on the cycle time of the reactor and is not improved or hurt by concentration of the feed.

- There are no tests with concentrated (filtered) feed. Since use of unfiltered feed would require a reactor with approximately three times the volume, this and most other processing options look more attractive with 10wt% solids than with the more dilute feed of approximately 3wt% solids. Because of the size of the Fenton's Reagent reactor, there may be even more reason to concentrate the feed, and foaming could be a greater problem when the solids are more concentrated.

- Residual solids remaining in the condenser and remaining on the glass wall of the reactor caused concern in the ORNL studies. If those solids contain significant organic carbon, they could be a potential problem for in-tank operations. For out-of-tank operations, solids accumulation may not be as serious a problem. It may only be necessary to insure that they will not hinder the operations in subsequent batches.

ITR Conclusions Regarding Fenton's Reagent

Fenton's Reagent has good capabilities to destroy organic compounds; its positive attributes include:

- It can operate at atmospheric pressure
- It operates below the boiling point of the liquid.
- There is considerable experience with the use of Fenton's Reagent for destroying other organic waste materials.

In summary, preliminary studies indicate that Fenton's Reagent is capable of removing the organic carbon from the radioactivity in the Tank 48 slurry , but one would be more confident after more tests are completed that better define all of the reaction products. Fenton's Reagent probably could be made to work. However, the large reactor volume, the high inventory of radioactivity in the reactor, the relatively sudden release of much of the available benzene, the increase in the waste volume, and the hazard of large-scale use of peroxide will be problems in the use of Fenton's Reagent technology.

4.5 Other Potential Candidates

The ITR survey of alternatives in Section 3 led to the more detailed investigations in the previous four sub-sections. These investigations led in turn to other options potentially important to the recovery of Tank 48. In this section, two of those are addressed:

1) Dissolving TPB for further reaction

2) Acid hydrolysis of TPB

Dissolving Precipitated TPBs for Further Processing

The ITR Team was favorably impressed by past initiatives at SRS that successfully decomposed NaTPB, and attempted to determine why the same ideas couldn't be applied to cesium and KTPB. Members of the WSRC staff advised that this was impossible because these latter two salts are insoluble. That raised the question of what could be done to make them soluble, and hence treated more easily.

The Team conducted preliminary experiments which showed that these salts can be dissolved, but that the solvents are unattractive for treating the bulk solution. The solvents tried are organic mixtures. Single solvents like acetone and alcohols do not work especially well: for example, the solubility of KTPB in 20% alcohol is only twice that in water. In preliminary experiments showed that both cesium and KTPB will dissolve in 25% acetonitrile-25% polyethylene glycol-50 % water at concentrations comparable to the dissolution of the corresponding sodium salt in pure water.

This solvent mixture potentially allows the potassium and cesium salts to be processed in the same way as the sodium salts. In other words, by adding organic solvents to Tank 48, the same process as used successfully in Tank 49 could be applied for Tank 48. However, this plus is balanced by significant minuses:

- The kinetics of decomposition, attractive for slow in-tank operation, are unattractive for the rapid decomposition for out-of-tank treatment.

- Adding organic solvents to get rid of a problem caused by other organic compounds is unattractive. Moreover, while polyethylene glycol is benign, acetonitrile, the scientific name for methyl cyanide, is not.

- Adding organic solvents doubles the volume which must be treated.

- More research and development would be required even if this option were without other handicaps.

The Team does not feel that this option should be pursued as the primary treatment technology of the Tank 48 cleanup. However, the Team does suggest a new strategy for removing the "heel," that is, the small residual solids left after Tank 48 is emptied.

Acid Hydrolysis

The ITR Team noted the number of careful studies that have been made at the SRS dealing with the decomposition in acid of TPB salts. These studies, performed at temperatures around 100°C and pressures less than six atmospheres, show substantial destruction of KTPB to benzene, phenylboric acid, and other organic species. These ideas are recognized to be impractical within Tank 48, because acid hydrolysis would cause excessive corrosion.

However, in a small tank, acid hydrolysis could be an additional route to destroying the contents of Tank 48. Available data suggest that copper catalysis would be especially effective, either in a series of stirred tanks or in a plug flow reactor equipped with a static mixer. Changes in pH should be accomplished with formic acid rather than nitric acid so that the volume of the salt slurry produced and sent to DWPF is not dramatically increased by the added sodium nitrate. This alternative is essentially the process used in the original Salt Cell in DWPF (this facility is no longer available for use). Also, the Small Tank TPB Precipitation process studied as part of the Alternate Salt Processing Project utilized this process. However, the complexity of the process removes it from consideration now as a rival for Steam Reforming, WAO, or Fenton's Reagent.

4.6 Aggregation for Direct Treatment of Tank 48 Waste

Aggregation is a processing alternative for Tank 48 wastes that involves blending recovered Tank 48 slurry with other SRS process wastes to form a combined waste stream that is suitable for processing into saltstone. Saltstone is made by blending the aqueous waste stream to be treated with a dry blend of Portland cement, blast furnace slag and coal fly ash to form a cementitious grout. The resulting material is pumped into an engineered reinforced concrete vault for disposal on-site. The grout cures to a monolithic, cementitious solid within the vault as the final waste form.

An important distinction between final treatment in DWPF and incorporation in saltstone is that the vitrified product from DWPF preserves the option for off-site disposal at a geologic repository, while saltstone would be disposed on-site at SRS. Aggregation is currently being carried as a back-up technology by WSRC, for application only if Steam Reforming and WAO prove to be unworkable.

Technical Overview

The composition of the filtrate to be processed into Saltstone is constrained to an activity of Cs-137 of less than 0.18 Ci/gal ($10.5x10^7$ dpm/ml), considering radioactive shielding requirements. Blending of the Tank 48 wastes (slurry contains $1.01x10^9$ dpm/ml) with other site wastes destined for Saltstone treatment can meet this criteria.

The state regulatory preference for off-site disposal vs. on-site disposal of the activity associated with the Tank 48 wastes is a policy decision, not a technical one. If the wastes are treated through aggregation to form Saltstone, future transfer to an off-site disposal location is not feasible, unless monolithic blocks are formed from Saltstone that facilitate retrieval rather than the planned vault design. Transfer of the radioactivity to a vitrified waste form through processing at DWPF results in a final waste form that is likely to be stored on-site for a long time period, but has the potential to be transferred for off-site disposal (e.g., at a geologic repository) some time in the future. Currently, such an off-site geologic repository is planned but not available.

The composition of material that can be currently processed into Saltstone is constrained to a concentration of TPB that is less than 30 Mg/L for processing from consideration of flammability hazards and to a concentration that is less than 10 Mg/Kg in the Saltstone product to insure meeting leaching criteria (toxicity characteristic leaching procedure, TCLP) as a non-hazardous waste under RCRA. Meeting the liquid feed concentration to Saltstone of less than 30 Mg/L insures attainment of the 10 Mg/Kg limit in the Saltstone product. (ref: discussion with Keith Liner, SRS with Independent Technical Review Panel on July 11, 2006).

Management of the potential for benzene evolution from a flammability hazard perspective during processing and disposal is planned to be addressed by (1) blending with other wastes to reduce the KTBP concentration to less than 3000 Mg/l (in contrast to the current KTPB concentration of 23,955 Mg/l in Tank 48 slurry), (2) upgrading the SPF by nitrogen inerting or ventilation improvements, and (3) upgrading the Saltstone disposal vault by installing a cover prior to Saltstone disposal and providing appropriate nitrogen inerting or ventilation in the Saltstone vault headspace. These approaches also facilitate management of the potential for benzene evolution causing an unacceptable atmospheric emission rate from the Saltstone processing or disposal vault. If needed, benzene destruction technology is readily available for treating contained process or disposal vault exhaust gasses (e.g., catalytic oxidation). Control of the KTPB concentration in the waste feed stream to Saltstone processing and the amount of waste slurry feed (loading) to the Saltstone product can be used to insure meeting RCRA land band and leachability criteria with respect to benzene.

Achievement of the criteria indicated above (e.g., TCLP) will satisfy regulatory and process safety requirements, but does not address the ultimate fate of the total quantity of benzene that potentially can be evolved during degradation of TPB during processing and Saltstone disposal. Some fraction of the benzene evolved during processing and disposal will be vented to the atmosphere or destroyed under controlled conditions (e.g., emission as a result of controlled ventilation to manage flammability hazards) and under uncontrolled conditions (e.g., low rate atmospheric emission during long-term decomposition in Saltstone). However, some fraction of the benzene has the potential to migrate to groundwater under the Saltstone vault, either through vapor migration or leaching pathways. Saltstone has no intrinsic chemical capacity to immobilize benzene and benzene is typically a persistent groundwater pollutant. The total amount of benzene that potentially may be evolved is approximately 19,000 Kg. The ITR Team also considers it prudent to minimize the amount of benzene that may be evolved in Saltstone after the initial curing period in the disposal vault. The fraction of this amount that potentially may migrate to groundwater, and associated consequences, has not been estimated nor could be estimated from the information provided to the ITR Team. This information needed includes thermodynamic variables like partition coefficients; dynamic parameters like rate constraints and diffusion coefficients; and geometric factors, like pore dimensions and architectures.

A careful evaluation is warranted to evaluate to potential for future groundwater contamination that may become a future restoration issue. Based on this evaluation, mitigation measures to minimize the risk of benzene introduction to groundwater most likely can be readily achieved through process design, Saltstone vault design and operational strategies. Thus, while this is an issue that should be evaluated and addressed, it is not considered a "show stopper" for use of aggregation as a process option.

Positive Attributes of Aggregation

Aggregation represents the Tank 48 waste processing option that can be implemented most rapidly if regulatory acceptance is achieved through policy decisions.

Technical Issues and Risks

The key technical issues and risks associated with this process alternative are:

- Reduction of Cs-137 activity in the waste feed stream to the Saltstone facility to achieve compatibility with existing saltstone facility shielding;

- Regulatory acceptance of aggregation is uncertain because of stated SCDHEC preference for off-site disposal of the radioactivity associated with the Tank 48 waste;

- Reduction of the potential for benzene evolution during processing and disposal to levels compatible with Saltstone processing from a flammability hazard perspective;

- Upgrading the SPF and disposal vaults to be compatible with potential benzene evolution during processing and curing from a flammability hazard perspective;

- Achieving reduction of potential evolution during disposal of Saltstone to meeting regulatory criteria with respect to benzene atmospheric emission rates and leaching criteria; and,

- Understanding the ultimate fate of the large quantity of benzene that may be evolved during (potentially long-term) degradation of TPB and the resulting potential for new on-site groundwater contamination. Design and operational strategies should be readily achievable to mitigate this risk.

ITR Conclusions Regarding Aggregation

The Team considers aggregation to Saltstone to be an appropriate back-up strategy for bulk Tank 48 waste material, provided that of the possibility of unacceptable levels of benzene contamination of groundwater from this process is satisfactorily resolved. The policy issues regarding disposal of significant quantities of Cs-137 on site would also require resolution.

4.7 Comparative Evaluation and Down-Selection

The ITR Team was asked to evaluate the options for treating the waste from Tank 48 and make recommendations regarding technology selection and implementation. In accordance with the ITR Charter, the Team placed primary attention on the methods currently in the WSRC path forward for Tank 48, specifically Steam Reforming and WAO, with aggregation as a back-up. The ITR Team also considered use of Fenton's Reagent, because there was additional interest in this approach.

The ITR Team concludes that all four of these processes can be made to work. The Team believes that Steam Reforming can be implemented most expeditiously because of its relative process maturity and design experience gained from the on-going design for the INL Steam Reforming facility. WAO is considered a promising back up process and a limited amount of additional research, as currently planned, should be completed to demonstrate whether or not the process is viable. Additional work on Fenton's Reagent is not warranted.

The rationale for these conclusions is summarized in the following sub-sections.

TPB Destruction

The basic objective of these processes is to destroy TPB salts, including that of Cs-137, into a stream containing inorganic salts and a stream containing most of the carbon. This is most easily described as two sequential steps. In the first, the TPB is destroyed; in the second, the carbon is separated.

The different schemes for destroying the TPB are compared in Table 4-2. The first column gives the variables which the Team considers most important. The second column gives values of these variables for an "ideal" reactor (an 'ideal' process is discussed in Section 2). For example, it is desirable for this reactor to quickly destroy the TPB at atmospheric pressure and modest temperature, producing only CO_2. The next three columns in the table give ITR Team estimates of the three reaction schemes.

Based on this comparison, Steam Reforming is the most attractive because it is fast and produces largely CO_2. It is the only method which has already been used with radioactive material, and so can be more easily implemented. One critical concern about Steam Reforming is the potential for uncombusted solid fuel to remain at unacceptably high levels in the solid product. The use of alternative fuel carbon sources to aid combustion – like sugar – hold promise to overcome this difficulty but remain to be demonstrated at sufficient scale and processing waste analogous to that in Tank 48. The Team thinks that this can be resolved but it needs to be demonstrated in planned pilot-scale testing at Hazen Laboratories. The product produced by Steam Reforming can be slurried and sent to DWPF.

WAO, also a strong candidate, directly produces a slurry that can, in principal, be directly fed to DWPF. However it involves high pressure of a radioactive waste in a three phase reactor, which does have a significant amount of liquid and gas under pressure. The reaction is slower. However, despite the slower kinetics, the WAO reactor may appropriately sized because the reactants are in a more dense liquid phase, rather in a gas phase. Important disadvantages of WAO are the high pressures required and that reduction of the TOC to levels compatible with DWPF processing have not been demonstrated processing waste analogous to that in Tank 48. Nevertheless, this may still be an attractive option if the organic compounds produced can be easily separated. The testing planned to be carried out at Zimpro during Fall 2006 should resolve these uncertainties and the viability of the WAO process.

Fenton's Reagent runs cooler and at one atmosphere. Now, however, the slow reaction risks explosion not from high pressure, but from peroxide. The neutralization dramatically increases the volume treated and the quantity of solids sent to DWPF. The Team views this as a poor choice relative to the others. The large reactor volume introduces problems with incorporation of equipment into the available space in the 241-96H facility, as well as the associated in-process inventory if radioactivity challenges efforts to maintain a modest safety category for the 241-96H facility. The use of Fenton's Reagent also increases the volume of the liquid waste and the subsequent volume of glass that would be produced from the waste.

These comparisons support the selection of Steam Reforming and WAO as the leading candidates. Fenton's Reagent is judged to be less attractive.

	METHOD			
VARIABLE	Ideal Technology	Steam Reforming	WAO	Fenton's Reagent
Reactor	Plug Flow	Fluid Bed	Bubble Column	Stirred Tank (batch)
Temperature	<200° C	680° C	200-300° C	<100° C
Pressure	<5 atm	1 atm	~100 atm	1 atm
Feed	>10% slurry	>10% slurry	>10% slurry	>10% slurry
	Soluble solid	Soluble solid	Aqueous slurry	Aqueous slurry
Carbon Fate	CO_2	CO_2, C, Na_2CO_3	Unknown (includes Benzene)	Unknown (includes Benzene)
Time, Reaction	<1 minute	~10 seconds	~1-hour	0(4-hours) ~12-hour cycle
Extra energy	None	Carbon as coke, sugar, or polyethylene	High Pressure	Hydrogen Peroxide
Problems	None	Form of added Carbon, uncertainty of residual carbon in solid product	Missing kinetics , limited data on composition of carbon in product	Reactor size, increase in waste volume, and limited data on kinetics and composition of product

Table 4-2: Chemical Routes for Destroying TPB

Carbon Product Processing

In addition to the reactions themselves, the carbon compounds which were expect to be produced were also considered. The results are given in Table 4-3.

	METHOD			
	Ideal Technology	Steam Reforming	WAO	Fenton's Reagent
COMPOUND				
Carbon Dioxide	Total	Most	(Major)	(Small)
Carbon Monoxide	None	Intermediate Only	(Small)	(Small)
Coke	None	In Solid Product*	None	None
Benzene	None	None	(Major)	(Major)
Phenol	None	None	(Small)	(Small)
Acetate	None	None	(Small)	(Small)

Note: Quantities in Parentheses are speculation.
* replace coke with sugar or other oxidizer

Table 4-3: Carbon Compounds Produced by Different Reactors

The first column in the table gives the compound. The second again gives an ideal: the Team would like all carbon released only as CO_2 or carbonate. Failing this, the Team would like all carbon released as benzene, which is relatively easily separated.

Again, Steam Reforming performs well: almost all carbon is released as CO_2. The exception, carbon particles in the solid product, potentially can be removed by changing the additional fuel fed to the reactor. Although changing the fuel used in a Steam Reforming reactor is expected to eliminate carbon in the product, demonstrating this should be a key goal of the next round of steam reformer tests.

WAO also appears to perform well, but the Team has less information on the residual organic constituents. If only benzene were produced, it can be treated easily, as explained in Section 4.3. If only carbon dioxide was produced, the ideal could be captured. If significant amounts of phenol and acetate were produced, processing would be more difficult. Fenton's Reagent is similar in this regard.

4.8 ITR Recommendations

Recommendation 4-1:

Steam Reforming should be designated as the primary approach for treating wastes from Tank 48. Pilot-scale testing should be used to demonstrate the ability of the process to achieve a solid product compatible with DWPF processing requirements. Preliminary design evaluation should be used to verify process compatibility with 241-96H facility constraints.

<u>Recommendation 4-2:</u>

WAO should be designated a back up process. The planned testing program for WAO should be continued only to the point necessary to demonstrate the process viability and effluent compatibility with DWPF processing.

<u>Recommendation 4-3:</u>

The requirements for the product from Tank 48 treatment to be acceptable as a feed stream to DWPF should be clearly defined.

<u>Recommendation 4-4:</u>

The potential for future benzene contamination at the saltstone disposal site, as a result of aggregation of Tank 48 bulk material or saltstone treatment of tank flush liquids or concentration filtrate should be evaluated.

<u>Recommendation 4-5:</u>

No further testing or evaluation should be pursued for Tank 48 treatment process based Fenton's Reagent chemistry.

5.0 Heel Management

There are multiple options for removing, concentrating, reacting and possibly relocating the bulk contents of Tank 48 as described in other sections of this report. No matter which options are selected a cross cutting issue is the necessity for nearly complete removal of the TPB solids in the heel after the bulk liquid is pumped out in order for the tank to be available for other service. At the same time, there is a goal to minimize the radioactivity retained in the State of South Carolina. To meet both of these objective, a series of tank flushes with varying liquids is recommended for this treatment. The TPB concentration in the flush effluent will be the indication of acceptable removal of TPB.

5.1 Heel Issues

Terms Defined

For clarity, three terms that will be used throughout this section to refer to the Tank 48 contents of at different phases of material removal:

- **Bulk** is the term for the portion of the original liquid in the tank which will be pumped out of the tank for further processing. This will be the slurry liquid from the current 68.5-inch level to as low as the 2-inch minimum pumping level. This is up to 243,000 gallons of slurry.

- **Heel** is the slurry liquid that remains after pumping the bulk liquid out of the tank. Except for difficulties with agitation which will be described later this liquid has the same composition as the bulk. This is a minimum of 7,000 gallons of liquid at the 2-inch level.

- **Residual**: after treating the heel with multiple washes and pumping the contents down to the lowest practical level, liquid will remain in the tank with a very low concentration of solids. This is the <u>residual</u> and will remain in the tank to be mixed with the material added to the tank in the normal service.

The Problem

Regardless of processing method or timing, a heel will remain after the bulk of the material is removed from the tank. This heel must be removed or treated to the point that the residual level of TPB meets acceptance criteria and is verified to be safe, before the tank can be put into its next service. Accomplishing that objective will be very challenging because:

1. The tank is large, it has few access points and its interior congested - and for those reasons, removal of the heel material will be difficult and, to some degree, incomplete.

2. The current criterion for TPB residual is unrealistically low. It is based on an extremely conservative assumption and compliance with it would require validation impossible to achieve.

Acceptance Criterion

The current undocumented criterion for Tank 48 return-to-service is that TPB content in the residual must be 12 Kg or less (personal communication, Renee Spires - WSRC). The lowest documented limit is 35 Kg [CBU-WPT-2005-00177]. This very low 12 Kg may be used as the acceptance criterion. This very low limit is based on the highly unrealistic scenario that in the new service (subsequent to bulk transfer and heel treatment) the entire amount of TPB remaining in the tank could be transferred to another tank and react instantly to form benzene, which would then accumulate in the non-inerted vapor space causing a flammable hazard. These assumptions are overly conservative and consideration is being given to raising the residual TPB limit (Renee Spires (WSRC) verbal discussion 6/21/2006). However, as discussed below, an alternative approach (rather than just a higher limit) may be needed.

5.2 Practical Considerations

Tank Configuration

See Section 2.1 for a description and schematic of Tank 48. Of most importance to the heel treatment question is that the tank is very large (85-feet in diameter and 33-feet high) and internally congested (containing about 4 miles of cooling pipes, four large slurry pumps, structural members, dip pipes and contaminated equipment that was purposely left in the tank).

Access for Inspection

Access to the Tank 48 interior is very limited, and visual inspection is further complicated by the physical configuration and congestion of the tank interior (i.e. .interferences with cooling coils, number of pumps and risers, etc.). Although limited visual inspections can be accomplished, there are not enough access points or clear passages inside the tank to be able to develop a full visual mapping of the tank contents in either an “as found” or “as left” condition.

Sampling of Contents

Representative sampling of the heel and residual is complicated by several factors. First, with the number of physical interferences in Tank 48, access to many areas of the tank interior is not possible. Second, the slurry pumps can only be operated with levels above 23-inches; once the tank level is reduced to that level, no further mixing of tank contents is possible. At that point the solids in the slurry will settle out in tank locations that cannot be reached by the transfer pump, leaving areas of concentrated material that cannot be sampled. Third, as mentioned in the previous section, without the capability to have full visual inspections, the volume and location of solids that have settled out in the tank cannot be accurately determined.

Tank Scale and Deposits

As reported in CBU-PIT-2005-00004, *Volume and TPB Content Estimate of Deposits on Tank 48H Internal Structures*, it was estimated that there are up to 33 Kg of TPB scale inside Tank 48 on the walls and internal components, mostly above the liquid level. A more recent communication, PIT-MISC-8181, *Thirteen Questions – Responses*, specifies using 1 Kg TPB for the scale quantity.

In discussions with WSRC staff, it was reported that film/scale on a thermowell was easily removed by soaking it in water. But when a transfer pump was removed and sprayed with 100 psi water there appeared to be a strongly adherent white-colored coating and that overall radiation readings were high. These readings were not investigated further to determine whether they were from localized hot spots in crevices, etc. or were just a result of the overall film/scale, and whether they would dissolve in other liquids.

5.3 A Proposed Approach for Heel Removal and Treatment

Tank 48 Heel Removal

As envisioned by the ITR Team, the removal of the bulk and heel from Tank 48 would best be accomplished by a regimen of pump out, re-fill, re-slurry and pump out as shown in Figure 5-1. The initial tank contents are approximately 250,000 gallons and the majority of this volume, the bulk, will be transferred and processed through one of the methods discussed in Section 4 and diagrammed in the upper section of Figure 5-1. The heel will then be treated through a series of flushes and analyses (as indicated in the logic diagram in the lower portion of Figure 5-1). The discharged flush liquid with low Cs and TPB content will be processed through Saltstone.

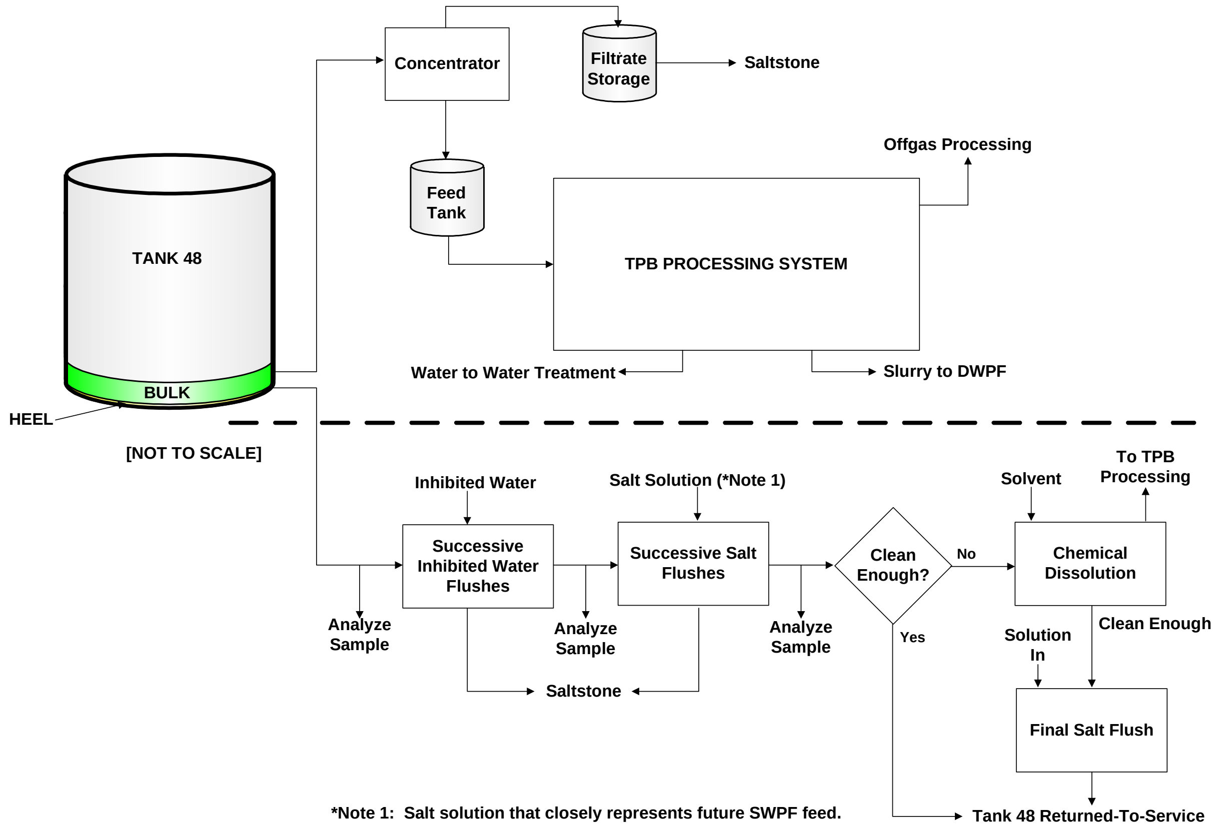


Figure 5-1: Tank 48 Bulk and Heel Treatment

Heel Flushing Sequence

Typically at SRS, cleaning of a tank heel to produce a residual that meets the required criterion is accomplished by adding inhibited water (IW) to the tank, agitating the mass to achieve suspension and pumping the liquid out of the tank. This is done repeatedly until the required end point is reached. The ITR Team plan for Tank 48 differs from this typical approach in that flushes with multiple liquids are proposed to take advantage of the relative densities of the Tank 48 solids and liquid and to provide higher confidence that any TPB remaining in the tank will not be released in any significant quantities during tank operations after its return-to-service.

The initial Tank 48 flushes would utilize IW. Once the analysis of the effluent from these flushes shows little or no TPB and Cs leaving the tank, these flushes will be discontinued. If the bulk liquid is being concentrated as described later in this report then the first wash should be sent through the concentrator also to be processed with the bulk material. This would remove a significant amount of TPB and Cs-137 from Saltstone and send it to the processing facility. The remaining IW washes would be sent to Saltstone.

Following the IW flushes, a series of high density salt solution flushes would be performed. The salt solution will be from the deliquification, dissolution, and adjustment (DDA) process or a synthetic salt solution of a concentration that is chemically and rheologically similar to the material to be introduced into the tank after return-to-service.

Use of the salt solution for flushes serves two purposes. First, due to the solution having a higher density than the TPB precipitate, some of the residual solids will be “floated”, thereby increasing the amount that can be mixed by the slurry pump mechanical action and potentially removing some of the heel that may have settled around the cooling coils. Second, because of the similarities of solutions involved, the flush effluent samples will serve as a realistic predictor of the amount of TPB that will be released, once the Tank is returned-to-service. The number of salt flushes will be determined by the analysis of the TPB and Cs in the discharge-that is, the flushes will continue until effluent TPB and Cs will be at a constant very low level (or non detectible).

The solid material has a low density and should float in denser liquids. This would greatly help the removal while the slurry pumps were operating but would be a detriment after they were shut down at 23-inches since the dip pipe would be drawing from the bottom of the liquid and the solids would be floating on the top. A skimmer type pump-out line which takes suction from the top or near the top of the liquid should be considered.

A final step for heel removal, if required, would be a series of chemical washes with a high vapor pressure organic material or mixture aimed at dissolving the remaining solids to achieve maximum cleaning and removal of the TPB. This step would involve introducing more organics into the process. If the chemical washes were necessary a last flush would be with salt solution to reduce the organic solvent in the tank. This material could possibly be processed through the TPB processing facility.

A high pressure water spray system can be employed to attempt to remove the scale in Tank 48 by washing all accessible tank walls and internals prior to the first IW flush. WSRC has substantial experience with these types of systems having used them in other tank cleaning operations, however, they may not remove the scale in this tank due to the interferences and inaccessible areas. A salt flush or IW fill to the previous high liquid level mark (159 inches) may be necessary

Confirmation to Standard

12 Kg of TPB - the current acceptance criterion for Tank 48 return-to-service - is equivalent to about 2.7 gallons of solids. In a tank the size of Tank 48, a final residual 2-inches deep would be 7,000 gallons of slurry. Given the limitations in access for sampling, the likely non-uniformity and non-homogeneity of the residual and the inability to mix it effectively, it would be essentially impossible to confirm that standard had been met. Even if the criterion were raised significantly - say by a factor of ten - it would be very difficult if not impossible to verify compliance.

Following the series of IW and salt solution flushes, and possibly a chemical cleaning, as described above, the only TPB remaining in the tank will be that which is either highly adherent or hydraulically inaccessible. While it may be impossible to measure precisely that remaining TPB quantity, it is very reasonable to assume that it will not be released in any significant quantity during subsequent operations after the tank is returned-to-service.

The ITR Team recommends that logic form the basis of a revised acceptance criterion for Tank 48 return-to-service. Specifically, the measured quantity of TPB in salt solution flush effluents, with adequate margin, should be used to conservatively predict TPB which can be transported during tank reuse after return-to-service, with supporting calculations to demonstrate that such TPB quantities cannot create downstream flammability or other hazards.

Schedule and Timing

Adequately removing the heel from Tank 48 will involve multiple flushes, storing and/or possibly synthesizing wash solutions, taking multiple samples and performing and reporting analyses. It is the opinion of the ITR Team that if these tasks are well planned, the duration for heel removal and Tank 48 cleaning, from the time the bulk liquid is pumped from the tank until the tank is returned-to-service, could be as much as six months.

5.4 Implications for Downstream Processing

The ITR Team recommends that the heel solid and wash material be treated via Saltstone. As described above, the Tank 48 heel will be treated by multiple washes with varying materials. Each of these washes will remove a small amount of K and CsTPB with a large amount of liquid. Processing this dilute slurry through the system chosen for bulk processing (regardless of which process method is chosen) would result in unacceptably large reactors or unacceptably long processing times (years), or both.

The exact amount of heel remaining is not known, but a very achievable split of 90/10 bulk/heel would reduce the amount of Cs-137 curies proportionally, that is to about 40,000 Ci to be sent to Saltstone. Similarly, the amount of benzene would be about 1940 kg rather than the 19,400 Kg that would be sent to Saltstone if the bulk of the tank contents were to be processed by Aggregation.

It is likely that the amounts sent to Saltstone would be even lower. For example, if the bulk can be pumped down to two inches, up to 97% of the curies could be removed and just 3% sent to Saltstone. The ITR team recommends pumping down to the lowest level practical, in order to minimize the waste burden on Saltstone, with the actual liquid volume and composition to be determined by the wash sequence and its effectiveness, as confirmed empirically from samples of wash effluent[11].

5.5 Recommendations on Heel Management

There are three primary ITR Team recommendations with respect to Heel management, as follows:

Recommendation 5-1:

The regimen of successive tank flushes using IW and then salt solution, as described in Section 5.3, should be adopted as the primary method for Tank 48 heel treatment.

Recommendation 5-2:

Concentrate the first flush of the heel to direct the curie content to Steam Reforming, and then to DWPF. This minimizes the curies stored in the Saltstone vaults. The remaining heel flush solutions would be processed to Saltstone.

Recommendation 5-3:

With respect to residual TPB, a fundamentally different acceptance criterion for Tank 48 return-to-service should be established. The ITR Team recommends that the approach outlined in Section 5.3 be adopted.

[11] As a point of reference, in the Aggregation Flow Sheet [CBU-PIT-2004-00012, Table 3] the amount of liquid to be processed in order to lower the TPB content from 1,434 Kg to 5 Kg was calculated to be 300,000 gallons. This serves only as a reference for the amount of heel to be processed to Saltstone since that flow sheet used only one wash fluid and assumed perfect mixing for the most part. Calculations with and without a high level flush indicate a range of 500,000 to 1,00,000 gallons respectively using a small correction factor to account for mixing efficiency.

In support of the above, the ITR Team identified four additional recommendations, as follows:

Recommendation 5-4:

A program to investigate materials that will dissolve the TPB and could be processed through the Saltstone system should be initiated, to accommodate the risk that the water and salt flushes are not sufficiently effective in achieving compliance with the TPB acceptance criterion established.

Recommendation 5-5:

The current scale and deposits on the internal components of the tank should be characterized to develop a better understanding of their long term adherence.

Recommendation 5-6:

Knowing whether the solids float or sink in the anticipated wash liquids is important towards planning the sequence. Some experiments to determine this property in IW, DDA discharge salt solution and simulated next service salt solution are recommended.

Recommendation 5-7:

Since the tank is large and there is no agitation at low levels, it is recommended that multiple draw off points at different elevations be used to pump out the slurry liquid as the solids may be buoyant in the salt solution.

6.0 Synthesis: The Integrated Solution

The previous sections of this report delineated the ITR Team's assessments, conclusions and recommendations regarding various elements of the Tank 48 path forward, including selection of an effective processing system, establishing an effective method to treat the Tank heel after bulk removal, and establishing a safe and achievable residual TPB acceptance criterion for Tank 48 return-to-service.

The ITR Team believes that its recommendations for each of these will significantly improve prospects for success, both in processing Tank 48 material and in returning the tank to service. At the same time, however, the Team remains convinced that the currently planned implementation strategy - that is, sequential material processing, heel treatment and tank cleaning - has very little chance of achieving Tank 48 return-to-service by the established need date of January 2010.

This section presents the ITR Team's evaluation and recommendations for an integrated application of the above steps in a way that reduces schedule risk inherent in the current approach and yields the best chance of achieving the January 2010 schedule.

6.1 The Current Strategy

The basic activities that must be conducted to achieve the combined objectives of Tank 48 return-to-service and the processing and disposition of the Tank 48 TPB-containing material are as follows:

1) <u>Obtain approvals and funding:</u> Put in place all needed program resources and approvals necessary to proceed.

2) <u>Engineer and build the TPB processing facility:</u> Design, engineer, procure, construct, startup and test the structures and systems required to process the bulk of the contents of Tank 48.

3) <u>Process the bulk of the Tank 48 contents:</u> Treat the bulk of the contents (90-97% of the contents by volume) to remove the TPB and any unwanted organic carbon leaving only the 2" heel in the tank.

4) <u>Treat the heel and clean the tank;</u> Through a series of IW and salt solution flushes, (and, if necessary, chemical cleaning) reduce the TPB in the heel to an acceptable level. This remaining, low concentration TPB material in Tank 48 is approximately the same volume as the heel (about 7,000 gallons) and is referred to as the "residual".

5) Demonstrate compliance with criteria for returning Tank 48 to service: When released for service Tank 48 will be used to store solutions as feed for Saltstone, SWPF or DWPF. Tank 48 must be demonstrated to have been cleaned to the degree that any remaining organic material in the residual is insufficient to contaminate the future feed from the tank to a level that could preclude processing in SPF, SWPF or DWPF.

The current WSRC plan is to conduct these activities in sequence.

6.2 Key Issues and Decisions

To execute this current strategy with best possible prospects for success, several key issues must be addressed and optimized decisions made. Most have been addressed previously in this report, as noted below. From that point, the larger question of how to achieve the return-to-service date of January 2010[12] must be considered.

TPB and Carbon Removal

The WAC for SPF, SWPF and DWPF are demanding with respect to TPB and elemental and organic carbon. Therefore, a very effective processing system to remove the TPB and carbon must be designed, constructed, tested and operated to meet the WAC. The ITR Team has recommended that Steam Reforming be adopted as the primary method for bulk processing, with WAO as the backup. (See Section 4)

Pre-Concentration of Processing System Feed

The TPB processing system (Steam Reforming, if the ITR recommendation is accepted) to be employed to separate the TPB and other organic carbon compounds from the bulk of the Tank 48 wastes must be sized to accommodate a number of constraints. It is desirable to locate this system in the existing 241-96H facility. Once sized for this facility, the process flow rate can be adjusted by raising or lowering the concentration of TPB in the feed to the system.

To minimize schedule risk, a one year processing time (with 50% downtime) is desirable. To achieve this, the feed concentration must be increased to about 10wt% or higher. The current solids percent of the Tank 48 contents is about 3wt%. Therefore these wastes need to be concentrated by a factor of more than three[13].

[12] The January 2010 return-to-service is called for in CBU-PIT 2006-00070, *FY06-FY12 SRS LW Disposition Processing Plan (DPP).*

[13] It is noted that the safety classification of Building 96H will dictate the total amount of radioactivity that can be present in the building at any one time, and this will in turn influence the acceptable combination of feed tank size and feed material concentration.

The technology for concentrating waste of this type at SRS is well understood and is mature. Cross flow filters have been used on other systems effectively and a filter can be designed to achieve the needed three times concentration of the bulk of Tank 48 wastes. In addition, recent tests of a rotary micro filter have demonstrated that it may be used effectively in this service. Tests are needed to demonstrate this filter performance with TPB-laden contents of Tank 48. However, these tests could be conducted in a short period of time that would not interfere with the schedule for the design, engineering and procurement of the concentration system.

The concentrate from this filter step would be forwarded to a feed tank for the Steam Reforming system and the filtrate can be pumped to Tank 50 where it will be prepared as feed for Saltstone.

Recommendation 6-1:

The ITR recommends that concentration of the contents of Tank 48 be increased to about 10 wt.% prior to storage and/or processing in the Steam Reforming system.

Heel Treatment

The ITR Team assessments, conclusions and recommendations with respect to (1) to reduce the TPB remaining in the heel in Tank 48, (2) the acceptance criterion for residual TPB to permit return-to-service, and (3) the disposition of Tank 48 flush solutions are presented in Section 5.

Schedule and Sequencing

The schedule challenge for return of service of Tank 48 by January 2010 is very demanding. Proven and practical systems and approaches must be employed and it is likely that accelerated efforts will be required to meet the deadline date.

To estimate the time needed for the systems and processing, the ITR Team used similar and recent project schedules (Actinide Removal Project (ARP) and Modular Caustic Side Solvent Extraction Unit (MCU)), which were done on a fast track basis. Typical durations for the common activities are:

- Design (conceptual to final) – 18-24 months
- Safety Analysis and Safety Evaluation Report – 12 months
- Procurement and delivery of equipment – 12 months
- Construction and assembly on site – 18 months
- Start up and test – 8 months

WSRC engineering, operations, project and planning personnel advise that the likelihood of being able to significantly reduce traditional time estimates to design, construct, start-up and test a new system is low. These durations are characterized as optimal, and so the ITR Team used them in its schedule analyses and comparisons.

Portions of these activities can be conducted in parallel. But overall, WSRC experience indicates that the composite duration of activities needed to process the Tank 48 bulk material would include four years to design, procure, construct, start-up and test the new system. Furthermore to achieve that schedule, the work must be expedited and be given the highest priority.

As shown in Figure 6-1 the time span to complete all the steps needed to achieve Tank 48 return-to-service, in the currently planned sequence, and using typical durations for critical path adjusted, is estimated to be 63 months. Starting the sequence in January 2007 would result in Tank 48 not being available before mid 2012. So conducting the activities in series does not come close to achieving the Tank 48 return-to-service date of January 2010.

The ITR Team notes that it is possible to improve upon this typical schedule for engineering, construction and start-up work. With early start, significantly compressed engineering schedule (based on work already accomplished in Steam Reforming), strong management and controls, and rapid turnaround on required permits and approvals – and no major upsets or delays – the team considers that the typical schedule can be improved by about a year. This “aggressive schedule” is also shown on Figure 6-1. Even with success to that degree, however, Tank 48 is not returned-to-service until more than one year after the January 2010 need date.

It is just as likely, however, that actual time to engineer, build, startup and operation the Steam Reforming system, and then to treat the Tank 48 heel and return the tank to service, will be longer than the typical schedule. The Steam Reforming system is new to SRS; the two major issues to be confirmed before proceeding are not trivial; the project will require substantial funding; the building constraints, system start-up and test and the initial operations present substantial challenges. The length of time added to the schedule because of these uncertainties could be very large.

In summary, the ITR Team believes the current sequential path strategy to be incompatible with the required date of January 2010 for Tank 48 return-to-service. A delay by more than one year is very likely, and by more than 2 years is very possible. A way to address the sequential schedule conflict is discussed in the Section 7.

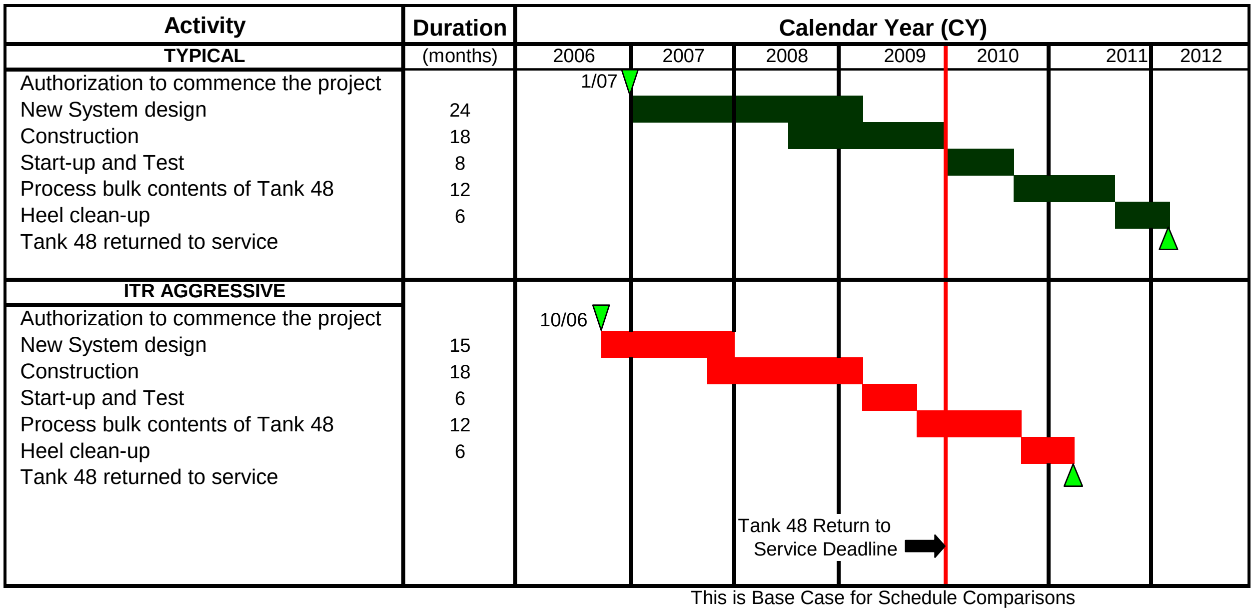


Figure 6-1: Sequential Schedule

6.3 Parallel Path: An Opportunity for Schedule Risk Mitigation

Conceptually, any project duration is driven by the critical path schedule. A schedule can be shortened only if one or more of its critical path activities can be shortened or taken off the critical path. The ITR Team believes that the activities required to achieve Tank 48 return-to-service lend themselves to such an approach, and that such a shift in implementation strategy offers the best opportunity to both achieve the needed tank availability schedule and reduce overall schedule risk.

In the current sequential schedule, the treatment of the heel cannot be accomplished until all of the bulk contents have been removed and processed (Figure 6-1). Furthermore this bulk processing can only occur after the new Steam Reforming system is designed, constructed and made operable. As described in the sections above, these activities carried out sequentially take a considerable amount of time (about five and a half years) and the schedule risk is significant because some SRS first-of-a-kind activities and other risks are involved. However, if the heel treatment work could be brought forward and completed while the Steam Reforming system is being built, or while the bulk contents are being processed, the Tank 48 return-to-service date could be brought forward 12 to 33 months depending on what tank space (existing or new) is used. Figure 6-2 is a conceptual comparison of sequential and parallel path approaches. Figures 6-2, 6-3 and 6-4 show the possibilities for schedule improvement.

The ITR Team has dubbed this schedule improvement option as the “parallel path” approach.

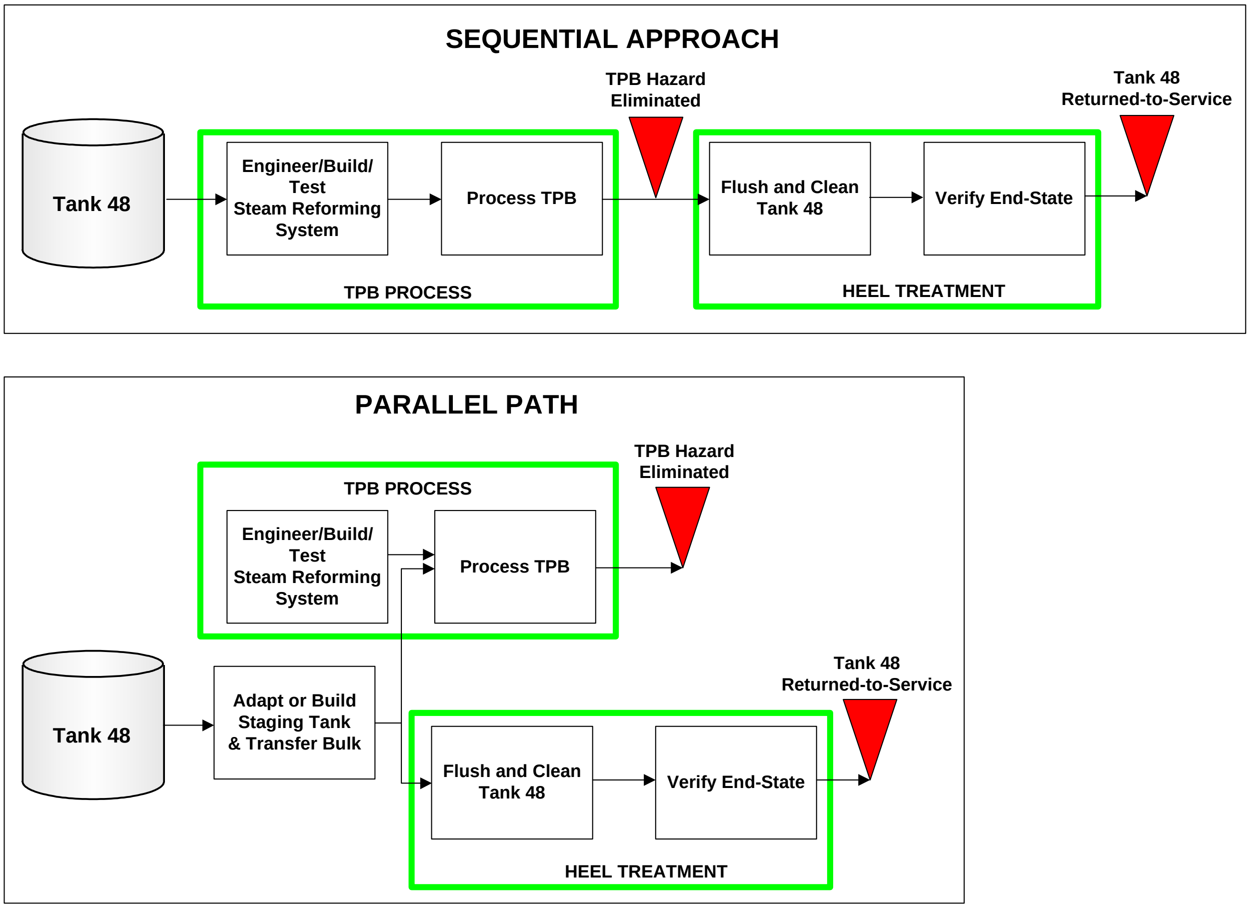


Figure 6-2: Sequential Path

Parallel Path Requires Tank Space

To accomplish this schedule reduction, tank space must be identified and utilized for temporary storage of the bulk of the contents of Tank 48. Once the bulk contents are removed the heel treatment and tank cleanup can be accomplished in parallel and independent of the processing of the bulk through the steam reformer (or other system, if selected).

Any interim storage or feed tank used for the storage of the bulk material from Tank 48 must be equipped to mix the contents and to control benzene that might collect in the vapor space of the tank. It also must include the system to concentrate the contents before feeding to the steam reformer or before storage. This equipment plus the piping needed to transfer the contents from Tank 48 to the interim storage tank, and piping necessary to transfer the contents from the feed tank to the steam reformer must all be installed, tested and declared operable. The ITR Team believes the schedule to accomplish these auxiliary system modifications can be considerably shorter than the schedule for building the steam reformer and processing the bulk of the contents in the sequential schedule. The waste transfer from Tank 48 to the interim feed tank is a short-term evolution (less than one month). Therefore Tank 48 could be made available for heel treatment long before the bulk treatment is completed and the overall schedule for Tank 48 return-to-service could be shortened accordingly.

This interim storage for the 243,000 gallons of waste from Tank 48 could be accomplished in either of two ways:

1. Use an existing waste tank retrofitted for the safe storage of the TPB wastes, or

2. Build a new qualified tank (or tanks) designed to accept and store the TPB wastes.

Existing Tank Space

The first alternative would be to transfer the bulk of the Tank 48 wastes to an existing tank modified with the necessary auxiliary systems. The WSRC 2006 Systems Engineering Study [G-ADS-H-00011] identified Tank 24 as the best option for this interim feed tank service. Tank 24 is a Type IV tank and using it to store this HLW would require acceptance from the stakeholders who are interested in closing tanks, not keeping them in service. Tank 24 is a single wall tank and the use for this waste would be a point of concern. Nevertheless, when considering the importance of the return of Tank 48 on schedule to support the broader mission of liquid waste disposition, the interim utilization of Tank 24 may make sense.

Moving the contents to Tank 24 appears to be straightforward. However the pumping from Tank 24 to 241-96H facility for processing does present some engineering and/or operational challenges. In all transfers special care must be used to ensure the organic compounds are not introduced to any other part of the tank farm systems.

In pursuing this approach, it should be confirmed that Tank 24 is the optimal storage tank for this purpose - and if not, another existing tank should be identified.

The ITR Team schedule assessment indicates that of the two alternatives, use of an existing tank offers the maximum schedule reduction and schedule risk mitigation opportunity. It appears that the deadline for Tank 48 return-to-service can be met with this parallel path option. See Figure 6-3. Note that the heel treatment consists of known methods and has substantially less risk than the processing of the bulk contents of Tank 48.

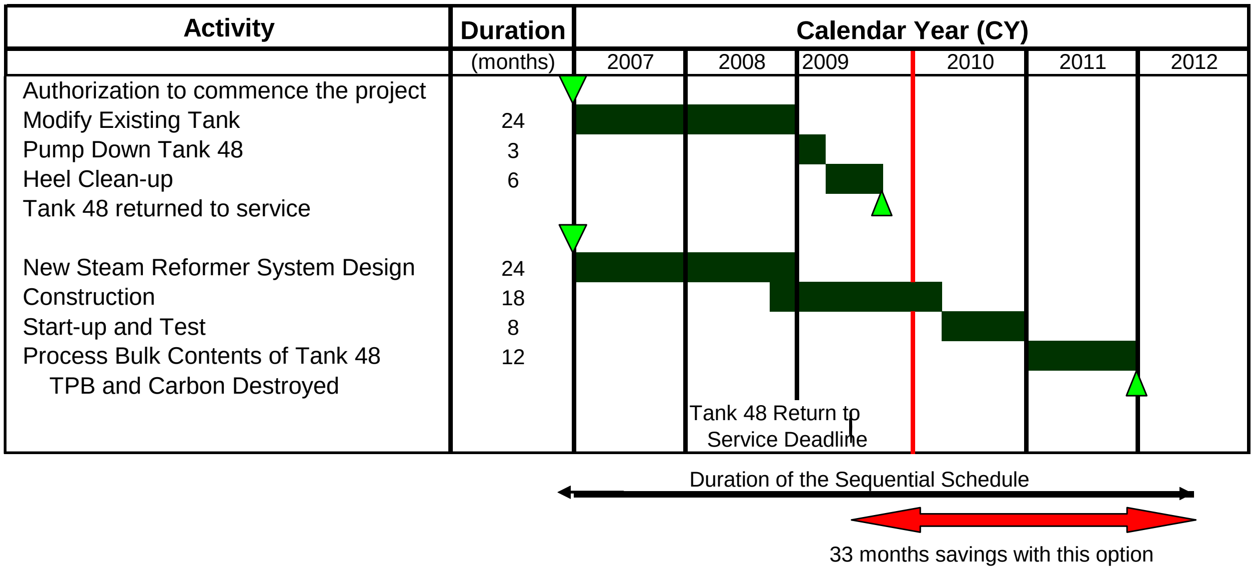


Figure 6-3: Tank 48 Parallel Path Schedule with Existing Tank

Construction of New Tank(s)

As an alternative to using an existing tank, one or more new tanks could be built and used for interim storage. The ITR Team explored the option of constructing a new tank dedicated to the interim storage of Tank 48 waste. Informal estimates from WSRC suggest that it would take 48 months to complete such a project. In that case, and assuming conservatively that the contents of Tank 48 could then be transferred to the new tank in three months, this parallel path approach could achieve Tank 48 return-to-service one year earlier than the ITR Team projection for the sequential option. On that basis, Tank 48 would be available in July 2011 - later than the established need date, but sooner than likely to be achieved by the current strategy.

But there is another option for building a new tank. WSRC is planning to build new tanks to support ARP/MCU and SWPF processing. Unpublished studies evaluating the need for lag storage volume for staging decontaminated salt solution feed to Saltstone to support MCU, ARP, and SWPF operation concluded that: (1) the use of Tank 50 as a feed preparation tank for the SWPF dictates the need for new tanks to serve as lag storage between the SWPF and Saltstone (SPF), and (2) this need would best be met by the addition of four 200,000 gallon tanks or two 200,000 gallon tanks and one 500,000 gallon tank. (The two options differ in cost and a selection decision has not yet been made, but in either case, two 200,000 gallon tanks would be built first.)

As envisioned by this draft study, one of the 200,000 gallon tanks would be built first and would be designed to initially support ARP/MCU operations. The other tanks would be built in time to support the later operation of SWPF. The study notes that the first tank could be constructed and made available within 21 months to support MCU operation beginning in the Fall of 2007. (Construction would need to start immediately to support this MCU schedule). This first tank would be built below grade and would be shielded for MCU/DSS discharge that contains 0.1 Ci/gal.

The ITR Team points out that if the Lag Storage draft study recommendations were to be adopted, the second tank could initially be dedicated to interim storage of the Tank 48 contents. This would require increased cost for the higher shielding requirements and nitrogen blanket system, and for a concentrator filter - but the incremental costs would be far lower than the total costs to build a new tank solely for Tank 48 interim storage.

The Lag Storage study indicates that the second tank can be completed within an additional six months, for a total of 27 months from the decision to proceed.

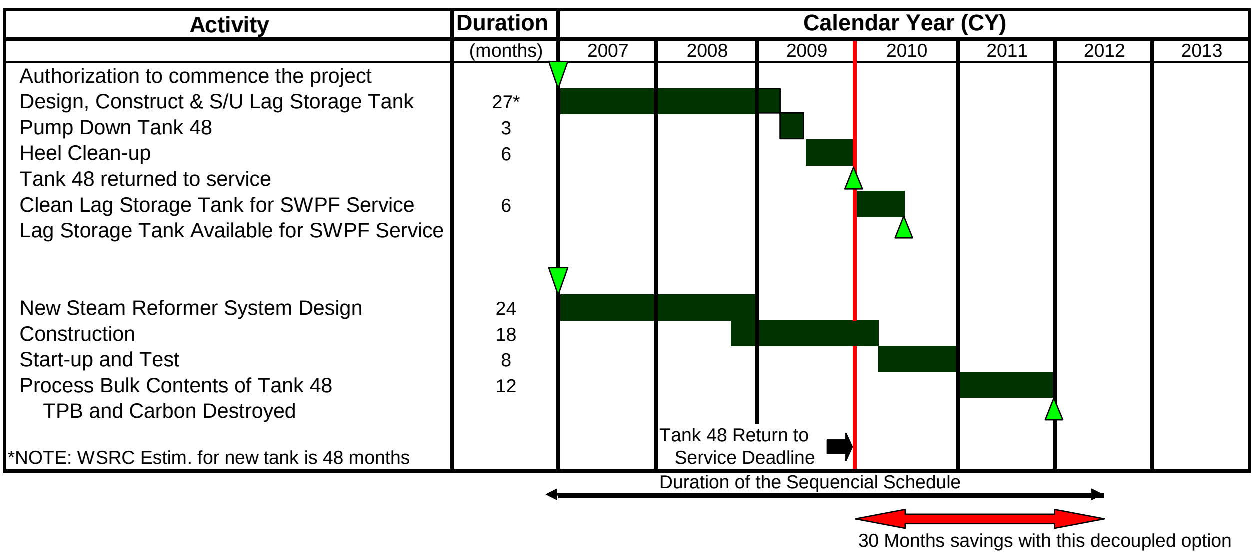


Figure 6-4: Tank 48 Parallel Path Schedule with Lag Storage Tank

Based on the Lag Storage study estimates, an interim storage tank could be available within 27 months or by March 2009, assuming a start date of January 2007. Assuming three months to transfer the contents to this tank and six months to process the Tank 48 heel (all assumptions consistent with previous schedule assessments), the tank could return-to-service by January 2010, in time to support the DPP.

After processing the contents of Tank 48 is complete, the tank could be cleaned and made available for SWPF lag storage. Unlike Tank 48, this tank could be designed for complete and efficient cleaning (by use of stainless steel construction, sloped bottom, and minimum internal interferences). The independent and parallel path processing of the Tank 48 contents would be complete near the end of 2011 or early in 2012 (See Figure 6-4) or, no later than early 2012, and the Lag Storage tank would be made available on time for its primary purpose, to support SWPF operation.

Building a new tank for two applications adds value to both. Financial resources are leveraged and total costs reduced. Moreover, stakeholder concerns that the new tank may become an indefinite parking place for an "orphan" waste (the Tank 48 bulk material) would be obviated by the certainty that the tank is needed for, and committed to, new service in the relatively near future.

For the new tank scenario to be viable, concentration of Tank 48 bulk material (as described in Section 6.2) is essential because it will reduce the size of the tank needed for the interim feed storage. Instead of a volume of 243,000 gallons, concentration to 10 wt.% results in a volume of about 80,000 gallons. Assuming that the first wash of the heel is also concentrated, a 100,000 gallon interim storage tank would suffice. Therefore, a 200,000 gallon lag storage tank would be adequate for this use.

6.4 Recommended Path Forward

In summary the ITR Team recommends as the composite path forward for achieving Tank 48 return-to-service by January 2010:

<u>Recommendation 6 -2:</u>

Adopt the parallel path strategy for achieving Tank 48 return-to-service by January 2010. As a first priority, evaluate and select the optimal interim storage location, either an existing tank or a new one (taking into account the implications and opportunities for each approach, as described in Section 6).

As a companion part of this recommendation, the composite path should include implementation of ITR recommendations in previous sections, including:

- Steam Reforming designated as primary processing method (Recommendation 4-1)
- Heel Removal regimen (Recommendation 5-1)
- Saltstone as disposition path for heel flushes (Recommendation 5-2)
- Pre-concentration of bulk (Recommendation 6-1)

7.0 Conclusions and Recommendations

7.1 Lines of Inquiry (LOI), and Conclusions and Recommendations for Each

The ITR Charter articulates the objective of the review effort in terms of very specific LOIs. These LOIs served as a basis for the Team's work, and conclusions regarding each can be found throughout this report. For clarity, the ITR LOIs, exactly as stated in the Charter, and the ITR conclusions and recommendations for each are tabulated below (Table 7-1).

Table 7-1: Conclusions and Recommendations

LOI-1: Validate completeness of Tank 48 alternatives evaluation: – Have evaluations of Tank 48 disposition actions considered a suitably broad range of alternatives? – Are there attractive alternatives, distinctly different from those already considered, which merit evaluation? – Identify any material differences from either a safe operations or regulatory envelope that could merit a different alternative solution.	
ITR Conclusions	– Sufficient processing options were identified and evaluated by WSRC to support full Tank 48 resolution, with no significant omissions. – More attention needs to be applied to integrated or composite options, including parallel path approaches. (See Section 5 of this report for further discussion in this area.)
Recommendations	None
LOI-2: Evaluate the treatment of uncertainty: – Have technical and programmatic uncertainties been adequately taken into account in Tank 48 alternative evaluations?	
Conclusion	Uncertainties have been fully considered and documented for some options (particularly Aggregation), and less methodically for others. But on balance, the Team concludes that the treatment of uncertainty was adequate for screening and relative merit evaluations.
Recommendations	None

<table>
<tr><td colspan="2">LOI-3: <u>Validate the down-selection process:</u>
– Are the selection criteria (including screening criteria and weighted evaluation criteria) sound?
– Where criteria have changed over the years, have previously rejected candidates been given sufficient re-consideration?
– Have the criteria been consistently and fairly applied?
– Were the evaluations performed in sufficient rigor to support valid conclusions?
– Does the set of alternatives currently remaining (i.e., not rejected from further consideration) support very high confidence in ultimate success?</td></tr>
<tr><td>Conclusions</td><td>– The WSRC evaluation utilized a strong, systems engineering process, well applied.
– Some inconsistencies among evaluations were noted, although not to a degree that undermined conclusions reached to date.</td></tr>
<tr><td>Recommendations</td><td>None</td></tr>
<tr><td colspan="2">LOI-4: <u>Assess the viability of the selected technologies and current path forward:</u>
– Is the current path forward (including preferred and backup paths) clearly defined?
– Is the current technical and project work adequate (in terms of definition, technical basis, planning, timing, adequacy of resources, etc.) to support the DPP schedule [CBU-PIT-2006-00070], process interface and performance needs?
– Are cost projections adequately bounded?</td></tr>
<tr><td>Conclusions</td><td>– Section 4 of this report is a comprehensive assessment of the technologies comprising the processing portion of the path forward; Sections 5 and 6 address cross-cutting issues and system and process interaction aspects.
– The Tank 48 processing portion of the current path is well defined; the path for heel removal and tank cleaning is being developed by WSRC but is not as well defined.
– There is not a detailed project schedule. In the ITR Team's view, the overall timetable for sequential processing, using either Steam Reforming or WAO, does not realistically support the January 2010 need date for Tank 48 return-to-service.
– There is not a detailed cost estimate breakdown for TPB processing or tank return-to-service. In the absence of a detailed plan, the Team was unable to assess current co evaluate the cost ranges currently assumed by WSRC.</td></tr>
<tr><td>Recommendations</td><td>– Select Steam Reforming as the processing method for the bulk contents of Tank 48, to allow undiluted attention to the development of that approach.
– Establish WAO as the back-up process; proceed with follow-on work only as necessary to confirm viability.
– If schedule adherence is considered essential, embark immediately on a decoupling approach, as recommended in Section 6 of this report.</td></tr>
</table>

<table>
<tr><td colspan="2">LOI-5: <u>Identify risks and assess adequacy of risk management actions:</u>
– Have the technical and programmatic risks associated with the current path forward been thoroughly evaluated?
– Are the risk mitigation actions (in place or specifically planned) appropriate for the identified risks?
– Are other risk mitigation actions recommended?
– Has the impact on downstream facilities been considered?
– Has the technical and programmatic risk assessment effectively accounted for the projected safe operations, maintenance, regulatory, process control and environmental risks and their mitigation?</td></tr>
<tr><td>Conclusions</td><td>– The technical risks associated with the leading processing technologies are generally well understood, and planned development and testing tasks are appropriate. The Team identified no insurmountable processing risks.
– There are several technical risks associated with Tank 48 heel management. The most significant of those is the near-certain inability to achieve the currently established limit on residual TPB (12Kg) prior to tank return-to-service.
– The ITR Team considers overall schedule risk to be very high - that is, it is very unlikely that the January 2010 return-to-service will be achieved in light of the number of significant technical challenges facing the tank processing campaign and the heel removal and tank cleanout campaign, and their sequential relationship on the critical path unless a parallel path approach is taken.</td></tr>
<tr><td>Recommendations</td><td>– Proceed on a high priority basis with the analytical work necessary to revise the acceptance criteria for residual TPB, based on the approach outlined in the ITR Report, Section 5.
– To mitigate schedule risk, put in place a high priority effort to define and implement the decoupling approach conceptualized in Section 6 of the ITR Report. (same as for LOI 5)</td></tr>
</table>

<table>
<tr><td colspan="2">LOI-6: <u>Evaluate treatment of constraints</u>
– Are there explicit constraints (technical, programmatic, regulatory, etc.) that influenced the screening or weighted evaluation of alternatives?
– Are these constraints well defined? Are they well understood? Do they have sound bases?
– Are there other unstated assumptions or presumed constraints which influenced the evaluation and selection of alternatives?</td></tr>
<tr><td>Conclusions</td><td>– The Team found instances of both explicit but unsupported constraints and other implicit but undocumented ones.
– On further review, the Team considered that these constraints were significant in previous evaluations and would continue to play a part in downstream implementation of a successful Tank 48 path forward</td></tr>
<tr><td>Recommendations</td><td>For ongoing and future work, establish a “constraint register” in a manner consistent with current practice vis-à-vis “risk register”. In the Constraint Register, identify each significant constraint and its basis, and establish the nature and limits of its application.</td></tr>
<tr><td colspan="2">LOI-7: <u>Evaluate the potential to re-solubilize the KTPB?</u>
– Does this option appear to have merit, based on lab testing and literature search?
– If so, what are its implications with respect to removal and disposal of Cs? Of benzene?</td></tr>
<tr><td>Conclusions</td><td>The ITR Team conducted extensive literature reviews and conducted some limited solubility tests; based on this the Team concluded that re-solubilizing the KTPB, while possible, is impractical because it requires addition of large quantities of organics to Tank 48.</td></tr>
<tr><td>Recommendations</td><td>None</td></tr>
</table>

<table>
<tr><td colspan="2">LOI-8: <u>Evaluate plans for Tank 48 cleaning and heel management</u>
– Are the criteria / standards for residual TPB content well defined? Well understood? Well founded?
– What methods (physical and chemical) are planned for tank cleanout? What is their expected effectiveness?
– How will residual TPB be measured?</td></tr>
<tr><td>Conclusions</td><td>– The residual TPB standards are well defined but unworkable, because of practical difficulty of tank cleanout (large area, limited access, high internal congestion) and low absolute value of allowable TPB (12 Kg, essentially not measurable).
– Tank cleaning methods are still being developed, but generally consistent with methods used (primarily flushing) for large tank cleaning at SRS and elsewhere.
– There is uncertainty and some inconsistency in available data regarding adherence of solids to internal surfaces in Tank 48.</td></tr>
<tr><td>Recommendations</td><td>– Develop and achieve acceptance on a revised approach for criteria for residual TPB (same as LOI 5)
– Place high priority on finalizing the approach for tank cleaning, and move forward with project planning; evaluate and apply the method proposed by the ITR Team (see Section 5)</td></tr>
<tr><td colspan="2">LOI-9: <u>Evaluate plans and practices for benzene management</u>
– Are current practices and future plans for handling benzene generated in the course of Tank 48 processing and material transfer appropriate and consistent with the hazard?</td></tr>
<tr><td>Conclusions</td><td>The ITR Team notes that the general practices employed at SRS to protect against flammability from benzene emission (both in the tank head space and other possible benzene release points) are more extreme than general practices in the chemical industry. However, they are consistent with DOE guidelines and requirements.</td></tr>
<tr><td>Recommendations</td><td>None</td></tr>
</table>

7.2 Overall ITR Results, Summarized

The Tank 48 ITR Team's evaluations, conclusions and recommendations are presented, in detail, throughout this report. Recommendations are highlighted and boxed for easy identification and clarity. They cover relatively narrow issues, such as the ITR Team's recommended flushing regimen for the tank heel, to very sweeping ones, such as the recommended change to the overall sequence (i.e., parallel path) of planned actions.

A fundamentally important observation offered by the ITR Team is that while selection of a TPB processing technology is important, it is only part of the problem. In the Team's view, the previous WSRC evaluations and selection of TPB processing methods have been thorough and have led to sound conclusions, but they have not fully addressed all of the issues necessary to achieve timely Tank 48 return-to-service.

The central objective of the SRS Tank 48 path forward is to return the tank to service in time to support the *FY06-FY12 Liquid Waste Disposition Processing Plan*, (DPP) schedule, which is, in-turn driven by FFA commitments for SRS tank closure. The DPP calls for availability of Tank 48 by January 2010.

It is the Team's collective judgment that January 2010 is <u>not</u> realistically achievable by the sequential processing approach currently envisioned by WSRC, utilizing either Steam Reforming or WAO as a primary processing technology. The Team believes that Tank 48 return-to-service by one year or longer after that date is a more likely outcome.

Recognizing that HLW processing plans involve some inherent unpredictability, it may be possible to meet IPP objectives with a Tank 48 return-to-service a year or more later than the currently projected need date of January 2010. The Team is not in a position to judge the implications or acceptability of a schedule slip of that magnitude; WSRC and DOE management must make that call based on regulatory, stakeholder and other programmatic considerations.

Based on the constraints of the established schedule and the Team's conviction that the current WSRC plan is unlikely to achieve that schedule, the ITR Team recommends that the parallel path be adopted. And noting that except for significant schedule risk the current plan is viable, the Team also offers an alternative recommendation for DOE and WSRC management consideration, should they be willing to accept that schedule risk.

In summary, the ITR Team recommends a Tank 48 Path Forward, as follows:

OVERALL RECOMMENDATION FOR TANK 48 PATH FORWARD

1. Regardless of strategy (sequential or parallel path):

   - Commit to Steam Reforming as the lead TPB processing approach, now; carry WAO as the backup processing approach, and conduct work as necessary to confirm viability (but no further, so as not to dilute the effort). ITR recommendations for Steam Reforming and WAO development and testing, consistent with this overall recommendation, are provided in Section 4 of the report.

   - Embark on high priority heel management project, including development, testing and planning for tank flushing, and establishment of a revised TPB acceptance criterion for tank return-to-service, both as outlined in Section 5 of this report.

   - Conduct a high-priority evaluation of concentration merits and methods for concentration of Tank 48 bulk; establish a pre-concentration sub-project accordingly.

2. To maximize the chances of achieving Tank 48 return-to-service by January 2010:

   - Adopt the parallel path approach outlined in Section 6 of the report.

   - Embark immediately on a high priority project first to select the optimal feed tank system (i.e., modification of an existing tank or construction of a new one), and then to implement that selection. This project will become the controlling activity on the critical path to Tank 48 return-to-service. Manage it accordingly.

   - Continue to develop and implement the Steam Reforming for TPB processing on the earliest practical schedule (to preclude the bulk Tank 48 material from becoming an "orphan" waste).

3. Alternative recommendation, if returning Tank 48 to service a year or more later than January 2010 is considered tolerable by DOE and WSRC management:

   - Continue with the present course (sequential strategy), with resource allocation and project management actions directed to addressing the Steam Reforming technical and programmatic risks and accomplishing the development work needed for rapid implementation of Steam Reforming at SRS, as outlined in Section 4 of this report.

Beyond this over-arching set of recommendations, the ITR Report includes numerous specific conclusions and recommendations regarding processing methods, heel management and cleanout, and other technical issues related to the tasks required to achieve Tank 48 return-to-service.

In summary, the ITR Team is confident that the TPB-contaminated HLW currently in Tank 48 can be safely and successfully removed and that the Tank can be returned-to-service. The actions needed to accomplish these tasks are well understood and fully within the capabilities of WSRC. The most daunting element of the job will be to meet the schedule constraints currently in place.

The ITR Team believes this overall job is manageable and technically achievable, with very high confidence, and that the SRS Team engaged in this work is fully up to its challenges.

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APPENDIX 1: CHARTER

[CBU-PIT-2006-00092, Rev. 1, *Planning Package for the Independent Technical Review (ITR) of the SRS Path Forward for Disposition of Tank 48*]

CBU-PIT-2006-00092
REVISION: 1

KEYWORDS:
Tank 48

RETENTION:
Permanent

CLASSIFICATION: N/A

Planning Package for the Independent Technical Review (ITR) of the SRS Path Forward for Disposition of Tank 48

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Prepared for U.S. Department of Energy Under Contract No. DE-AC09-96S

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Revision Summary

1.	Document and Revision Numbers: CBU-PIT-2006-00092 Rev. 1
2.	Document Title: Planning Package for the Independent Technical Review (ITR) of the SRS Path Forward for Disposition of Tank 48
3.	Effective Date: 06/19/2006
4.	Document Changes: This revision includes a change to the original Line of Inquiry No. 6, and adds Lines of Inquiry 7-9, as shown on page 10. These revised and new Lines of Inquiry were developed by the Tank 48 ITR Team members at the conclusion of the first week of presentations, discussions, and reviews of the documentation regarding previous technology evaluations.

Introduction and Overview

As directed by the US Department of Energy (DOE) (References 1, 2) the Washington Savannah River Company (WSRC) is preparing to engage a team of independent technical reviewers to assess SRS consideration of alternatives and selection of preferred methods for disposition of the tetraphenylborate (TPB) contamination and restoration of Tank 48H to service (Reference 3). The purpose of this document is to present, for DOE information and approval, the planned approach and process for organizing, staffing and conducting this review.

The proposed specifics for the Tank 48H Independent Technical Review (ITR) are provided in the appendices to this planning document, as follows:

- Attachment 1 - Charter, including the initial Lines of Inquiry
- Attachment 2 - ITR Skill Matrix showing the linkage between Lines of Inquiry and the capabilities needed to address them
- Attachment 3 - The Prospective ITR members with their credentials and areas of expertise, cross-referenced to the Skill Matrix.
- Attachment 4 – Proposed path forward for the review, including preparation, approval and implementation

Planning and Preparation

4. Overall Process

The process will follow the overall guidance provided by DOE (see General References, pg. 6) regarding conduct of "Best and Brightest" reviews, with refinements as needed to accommodate the unique aspects of this review[14].

It is anticipated that the Tank 48 Independent Technical Review (ITR), from kickoff through delivery of final report, will require about ten weeks, although the actual duration will be dictated by the ongoing course of work. The review activities will include technical briefings by and discussions with SRS personnel, tours of the pertinent facilities and equipment, reviews of technical documents and data, and the like. A very significant contributor to the effectiveness of this review will be the synergy and interaction of the knowledgeable, independent subject matter experts (SME), and it is expected review team interactions may prompt some changes to the initial plan and schedule for the review.

5. Scope Definition

As stated in the Charter, the scope of this review is basically two-fold: first, to assess the collective completeness and validity of the evaluations of Tank 48H alternatives conducted since 2003, and secondly to evaluate the viability and risk management implications of the current path forward for approaches currently being considered. Lines of inquiry have been prepared (and are part of the Charter) to support a methodical, structured execution of this scope.

[14] It is noted that the TANK 48H review was initially conceived and planned as a WSRC-managed independent review, and for that reasons the initial preparatory work was started with routine DOE involvement. Subsequent to receipt of DOE direction (reference a), the process was revised to incorporate DOE guidance and approval.

A key element of the strategy for this review is to leverage the team members' experience and expertise to determine which specific technical issues, obstacles or decisions warrant the closest examination. To that end, the initial review phase will be dedicated to developing sufficient collective understanding by the team of Tank 48H issues and then to jointly develop, as appropriate, additional or expanded lines of inquiry to address key areas. That outcome will influence subsequent team activities, schedule and resources.

6. Organizational Role and Responsibilities

This review will be conducted under the overall direction of DOE, and for that reason, this plan, the Charter, Review Team membership and the review schedule all require DOE approval. As appropriate, contracting officer authorization may also be required for the work to proceed.

Upon authorization and approval of the review documents noted above, the Review Team activities will be managed by the Review Team Leader, with technical, logistic and administrative support from WSRC, as outlined below. The WSRC Executive Vice President has overall responsibility for the timely and effective completion of this work; the Team Leader will keep him fully apprised.

7. Selection of Team Members

A slate of candidate review team members was developed with input from a variety of sources, including lists of participants in other independent reviews (notably, the recent Waste Treatment Plant (WTP) review at Hanford), recommendations from SRS contractor and DOE personnel, and networking (including recommendations from other candidates, based on discussions about the scope of work). Following a review of their credentials and experience, discussions with individuals with personal knowledge of candidates' capabilities, and telephone discussions with those considered most likely to meet the needs of the Tank 48H review process, the prospective team members were selected.

Criteria for selection were as follows:

1. Clear alignment between the individual's credentials and experience and the needs of the review, as defined by the Charter and Lines of Inquiry (LOI).
2. Unquestioned independence, as defined in the charter. (On this point, prior knowledge or experience with SRS was not considered a disqualifier, provided that the individual has no vested interest, inclination or incentive to produce anything other than a 100% objective and detached evaluation.)
3. Strong interest and willingness to participate.
4. Reasonable expectation of availability.

Note that the selection process requires consideration of not only individual credentials but also the capability of the composite team. The selection included consideration of team balance with respect to technical, management and operational skills.

Further, in selecting team members, we have relied heavily on feedback from others regarding contribution of various candidates in other comparable review efforts. In that respect, the WTP experience was considered very valuable and was a significant factor in narrowing the proposed membership to the current list.

DOE approval of all members will be secured prior to start of this review. Contracts have already been let in some cases to allow initial review and critique of technical documents. If any individual already contracted is not ultimately selected by DOE, that contract will be canceled.

Attachment 2 to this document illustrates the Lines of Inquiry matrixed to the skill sets which support the review. Attachment 3 provides an index of the proposed review team members with a summary of their skillsets with which they best support the review matrixed to the LOI skill sets.

It is anticipated that during the course of the review, the need for additional specialized expertise may be identified. In that case, supplementary team members (probably with limited scope of involvement) will be proposed for DOE approval.

8. Stakeholder participation

In the interests of achieving full confidence in the outcome of this review, it is intended that the review process will be fully transparent. DOE, DFNSB and SC DHEC have been invited to assign representatives to observe the review process, and those representatives are welcome to attend all ITR activities.

9. SRS Support

WSRC will provide ongoing support to the ITR in several areas, as follows:

DOE-SR Point of Contact (POC):
Doug Hintze, Director, Waste Disposition Programs Division (doug.hintze@srs.gov 803-208-6076, pager 18989) will serve as the primary point of contact between the ITR and DOE.

WSRC Contracts

Bob Walter (robert.walter@srs.gov, 803-952-6161, pager 17439) is the WSRC Procurement & Materials Management Department Manager assigned responsibility for contractual aspects of this work

WSRC Management

Bill Van Pelt (bill.van-pelt@srs.gov, 803-208-8327, pager 11104) has been assigned to represent the SRS LW Chief Engineer in all respects during the course of this review, and will be available to assist in resolution of issues requiring management action.

WSRC Technical Liaison

Bob Hinds, SRS Engineering Project Manager (robert.hinds@srs.gov, 803-208-3473, pager 17549), has the lead for technical support for the ITR team. Bob will set up meetings and briefings and he will provide review materials and other resources. He will be the primary point of contact for follow-up and resolution of team members' technical questions and for arranging technical interactions with SRS personnel.

WSRC Administrative Support

SRS will provide support to the team and to individual team members re conference room, computers, phone messages, typing, copying, travel arrangements, etc.

WSRC Document Services

SRS will provide technical writing, report production and presentation material preparation support, as needed.

Working Space

It is anticipated that most team meetings will be held at an off-site location in Aiken, and that additional working space, computer terminals and telephones will be available for team members' use in report preparation and other team-support activities.

REFERENCES

1. Letter, W. F. Spader to R. A. Pedde (SPD-06-150), "Tank 48 Recovery," dated 5/11/06.
2. Letter, T.J. Spears to W.G. Poulson (WDPD-06-104), "Best and Brightest Review of Liquid Waste Disposition Program," dated 4/6/06.
3. Letter, W.G. Poulson to T.J. Spears (LWO-2006-0006), "Best and Brightest Review of Liquid Waste Disposition Program, dated 4/13/06.

GENERAL REFERENCES

The following general references were used in the development of the Planning Package and Charter:

1. E-mail, Gilbertson to Hintze, 4/25/06, forwarding e-mail from Dr. David Kosson, Ph.D., Vanderbilt University, to Joel Case, Subject: Steam Reforming, dated 4/25/06, attachment, "Scope of Work."
2. Demonstration Bulk Vitrification System External Flow sheet Review (Known as Best and Brightest Review) Charter, Approved by Roy Schepens, 3/31/06.
3. E-mail, Kaltreider (DOE) to Spears, et al, SRS Waste Processing B&B Comments, 4/21/06, with attachments, 1) "Draft Issues for Best and Brightest Technical Reviews," 4/17/06; 2)"Draft Action Plan for Best and Brightest Reviews," 4/17/06; and 3)"Key Attributes of Technical Review Process," 4/10/06.
4. Presentation, Tamosaitis to U.S. DOE, April 18, 2006, "An Overview of the WTP B&B Review" (lessons learned).
5. "Key Line of Inquiry, Best and Brightest Technical Review ORP Demonstration of Bulk Vitrification System," 4/26/06 Draft.

Attachment 1: Charter

Independent Technical Review (ITR) of SRS Path Forward for Disposition of Tank 48

Overview

WSRC will convene an independent technical review of key aspects of the selected path forward for disposition of the tetraphenylborate (TPB) contaminated radioactive waste in Tank 48 and for the tank's return to service. The object of the review is to validate the completeness and validity of the systems engineering process used to select the path forward, and to confirm the viability of the technologies selected as the preferred and back-up options. This review is also intended to identify technical and programmatic risks and uncertainties with the selected path, and to determine if these have been thoroughly examined and countered with effective mitigation strategies.

The results of this review will be used as one basis for finalizing the selection and proceeding with project activities to design, construct, and operate the engineered systems required to restore Tank 48 to service for radioactive waste processing.

Background

- Tank 48 contains 250,000 gallons of legacy salt waste that is contaminated with approximately 19,000 Kg of organic Tetraphenylborate compounds from operation of the In-Tank Precipitation process. This material must be removed or treated to allow for return of Tank 48 to general Tank Farm service.
- Four Alternative Treatment Evaluations have been performed since 2002. Each evaluation was performed using a Systems Engineering Evaluation Process as depicted in Figure 1 (page 12). The results of each evaluation are shown in Figure 2 (page 13).
- The top treatment options identified by the 2006 evaluation are Aggregation, Wet Air Oxidation, and Fluidized Bed Steam Reforming. These options are being developed.
- A Letter of Direction from DOE-SR to WSRC (SPD-06-0150, Spader to Pedde, Subject: Tank 48 Recovery, dated 5/11/2006) was issued to change Aggregation from the baseline option to a back-up. This letter also authorized testing for the two alternative options identified above and directed WSRC to complete the on-going systematic evaluations and submit a recommendation for Tank 48 material treatment.

Current Status of Options

- **Aggregation**
  - Since this was the baseline for treatment of Tank 48 material, there has been an active project for design and construction of the modifications required.
  - Design is 75% complete, construction is 30% complete. Startup was planned for 3/07.

- **Wet Air Oxidation**

  – The WAO process is based on oxidizing the waste at high temperature (200-300^{o}C) and high pressure (1,000-2,000 psi) to destroy the organic.
  – The by-products are: (1) treated liquid waste that can be returned to the Tank Farm and eventually be dispositioned as vitrified glass, and (2) an offgas stream that can be filtered and exhausted to the atmosphere.
  – Procurement has been initiated to test Tank 48 simulated waste at a vendor bench scale test facility with testing to complete by 9/06. A vendor site visit is planned.

- **Steam Reforming**
  – The FBSR process is based on pyrolyzing the waste at high temperature (600-900^{o}C) and ambient pressure in an environment with insufficient oxygen to support combustion to destroy the organic component.
  – The by-products are (1) solids containing Cs-137 that can be dissolved and returned to the Tank Farm and eventually dispositioned as vitrified glass, and (2) an offgas stream that can be filtered and exhausted to the atmosphere.
  – FBSR was tested in crucibles at the SRNL as well as in a pilot plant using Tank 48 simulant as part of an earlier evaluation. Although technically feasible, this option was eliminated at that time due to the processing capacity/rate required and its associated cost.
  – Additional bench scale testing will be performed this summer.

The purpose of this initiative is to review these evaluations for completeness and validity, and to confirm the viability of the current path forward. As part of that task, the review team will identify technical or programmatic risks, if any, that could jeopardize the return to service of Tank 48 by the projected need date.

To accomplish this objective, the team will review existing documentation of SRS Tank 48 evaluations, with particular attention to the comprehensive Systems Engineering study "Tank 48 Return to Service," Report No. G-ADS-H-00011. This study identifies the preferred technology and two back up strategies that will be a major focal point of this Independent Technical Review (ITR). Four previous studies and a risk assessment will serve as the basis for the Tank (ITR). The documents containing the results of these studies and the risk assessment are:

- G-ADS-H-00011, Liquid Waste Disposition Projects, Tank 48 Return to Service Systems Engineering Evaluation, 4/2006
- CBU-PIT-2005-00147, Re-Evaluation of Tank 48H Disposition Alternatives, 7/2005
- Y-RAR-H-00057, Tank 48 Disposition Project Risk Analysis Report, 5/2005
- G-ADS-H-00007, WSRC In-house Treatment Option Evaluation, 2/2004
- WSRC-RP-2002-00154, Rev. 1, HLW Tank 48H Disposition Alternatives Identification, Phase 1 & 2 Summary Report, 7/2002

Scope and Lines of Inquiry

The scope of the ITR has been defined in the form of lines of inquiry (LOI) that will serve as the framework for review team activities and for selection of review team members. These are:

1. Validate completeness of Tank 48 alternatives evaluation:
   - Have evaluations of Tank 48 disposition actions considered a suitably broad range of alternatives?
   - Are there attractive alternatives, distinctly different from those already considered, which merit evaluation?
   - Identify any material differences from either a safe operations or regulatory envelope that could merit a different alternative solution.

2. Evaluate the treatment of uncertainty:
   - Have technical and programmatic uncertainties been adequately taken into account in Tank 48 alternative evaluations?

3. Validate the down-selection process:
   3.1. Are the selection criteria (including screening criteria and weighted evaluation criteria) sound?
   3.2. Where criteria have changed over the years, have previously rejected candidates been given sufficient re-consideration?
   3.3. Have the criteria been consistently and fairly applied?
   3.4. Were the evaluations performed in sufficient rigor to support valid conclusions?
   3.5. Does the set of alternatives currently remaining (i.e., not rejected from further consideration) support very high confidence in ultimate success?

4. Assess the viability of the selected technologies and current path forward:
   4.1. Is the current path forward (including preferred and backup paths) clearly defined?
   4.2. Is the current technical and project work adequate (in terms of definition, technical basis, planning, timing, adequacy of resources, etc.) to support waste disposition processing plan (DPP) schedule, process interface and performance needs?
   4.3. Are cost projections adequately bounded?

5. Identify risks and assess adequacy of risk management actions:
   5.1. Have the technical and programmatic risks associated with the current path forward been thoroughly evaluated?
   5.2. Are the risk mitigation actions (in place or specifically planned) appropriate for the identified risks?
   5.3. Are other risk mitigation actions recommended?
   5.4. Has the impact on downstream facilities been considered?
   5.5. Has the technical and programmatic risk assessment effectively accounted for the projected safe operations, maintenance, regulatory, process control and environmental risks and their mitigation?

6. Evaluate treatment of constraints
   – Are there explicit constraints (technical, programmatic, regulatory, etc.) that influenced the screening or weighted evaluation of alternatives?
   – Are these constraints well defined? Are they well understood? Do they have sound bases?
   – Are there other unstated assumptions or presumed constraints which influenced the evaluation and selection of alternatives?

7. Evaluate the potential to re-solubilize the K-TPB and Cs-TPB
   – Does this option appear to have merit, based on lab testing and literature search?
   – If so, what are its implications with respect to removal and disposal of Cs? Of benzene?

8. Evaluate plans for Tank 48 cleaning and heel management
   – Are the criteria / standards for residual TPB content well defined? Well understood? Well founded?
   – What methods (physical and chemical) are planned for tank cleanout? What is their expected effectiveness?
   – How will residual TPB be measured?

9. Evaluate plans and practices for benzene management
   – Are current practices and future plans for handling benzene generated in the course of Tank 48 processing and material transfer appropriate and consistent with the hazard?

Period of Review

It is anticipated that the Tank 48 ITR will begin on or about 6/6/2006 and that a final report will be delivered on or about 8/10/2006. The results of the Tank 48 review will serve as input to an anticipated follow-on ITR of Liquid Waste Disposition Processing Plan, to be addressed in a separate charter. A detailed schedule for the Tank 48 ITR subsequent meetings, individual assignments, and production of the report will be developed as a product of the initial one-week meeting.

Team Structure and Membership

In composite, the independent review team will comprise expertise and extensive experience in design, engineering and management of chemical processing and radioactive waste management systems. The team will include approximately ten independent experts whose credentials and experience align with the specific lines of inquiry listed above and who collectively provide to the team sufficiently broad capability and flexibility to address the full range of issues that may emerge in this review. The experts will be independent of any corporate accountability or responsibility for managing Tank 48 return-to-service or for selection of the preferred technologies, and they will be free of any conflict-of-interest with respect to potential benefit from the selection of any specific technology.

Specific responsibilities will be as follows:

Review Team Leader

The Review Team Leader will be a member of the team and will have overall responsibility for preparation, scheduling, organization and execution of review team activities. The team leader will identify needed technical support including presentations, and supporting documentation. The review team leader will set the overall working schedule, and will facilitate team meetings, will lead the preparation and delivery of progress reports, will facilitate issue resolution and will coordinate and guide the structuring and preparation of the team report.

The Review Team Leader, assisted by the Technical Lead, will be responsible for managing the logistics of the review team effort, providing or arranging for needed administrative support, assisting the team leader in report and presentation production, and the like.

The Review Team Leader will ensure that DOE-HQ, DOE-SR, DNFSB, SC DHEC, and WSRC Liquid Waste Operations senior managers are notified of key meetings and summary progress reports.

Independent Technical Review (ITR) Team Members

Each team member is responsible for conducting a thorough, professional and independent review, for supporting the identification and resolution of technical issues, for participating in the development of draft and final reports, of supporting resolution of comments and any points of disagreement. Collectively, the team is responsible to produce a high quality review report that is responsive to this charter, that includes unambiguous conclusions regarding the identified LOIs, and that presents clearly any dissenting viewpoints. All team members will sign the final report.

WSRC Executive Vice-President

The WSRC Executive Vice-President is responsible for the efficient and timely execution of the DOE-approved ITR. He will work with the Review Team Leader to assure that current project information is made available to the review team, and that key members of the project technical staff are made available for reasonable interaction with the various teams so that technical information, responses to questions, and clarification of issues can be achieved efficiently.

DOE-SR

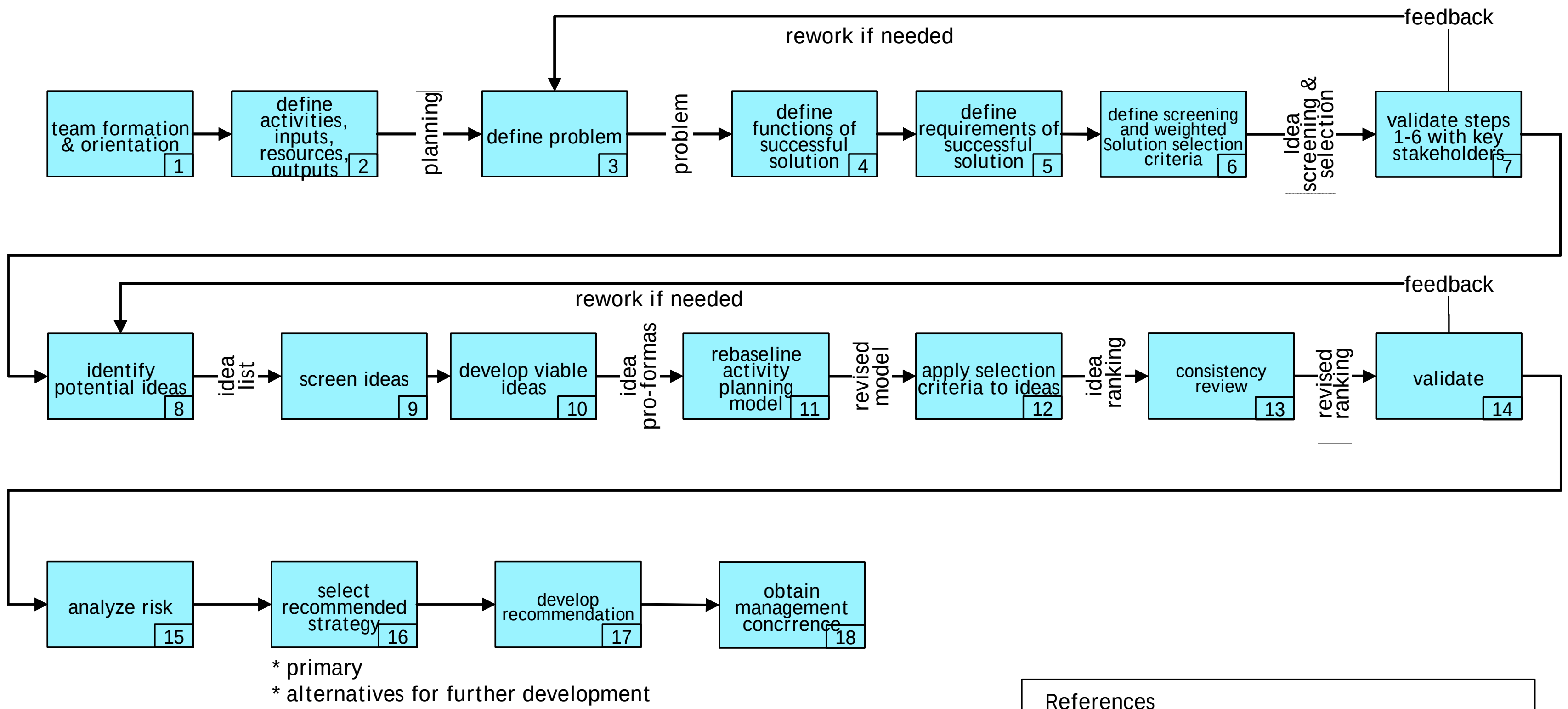
DOE-SR shall review and approve the Tank 48 ITR Charter (with Lines of Inquiry) and the ITR team selection, and will obtain DOE-EM HQ concurrence as necessary. DOE-SR will participate as an observer during the various meetings and progress reporting, will review the interim draft and final reports, and provide comments to the Team Leader in a timely fashion. DOE-SR receives the final output from the ITR, as the primary customer.

DOE-EM HQ

DOE-EM HQ shall review and concur with TANK 48 ITR Charter (with Lines of Inquiry) and the ITR team selection. EM HQ staff may participate as an observer in the various meetings and progress reports. EM HQ will assure necessary communication with other EM entities that have an interest in the progress and outcome of this review, and will arrange for any necessary EM briefings or meetings that may be required.

Tank 48 Systems Engineering Planning Model

Figure 1.



References
* E7 Procedure 2.13
* Systems Engineering Manual, WSRC-IM-980003

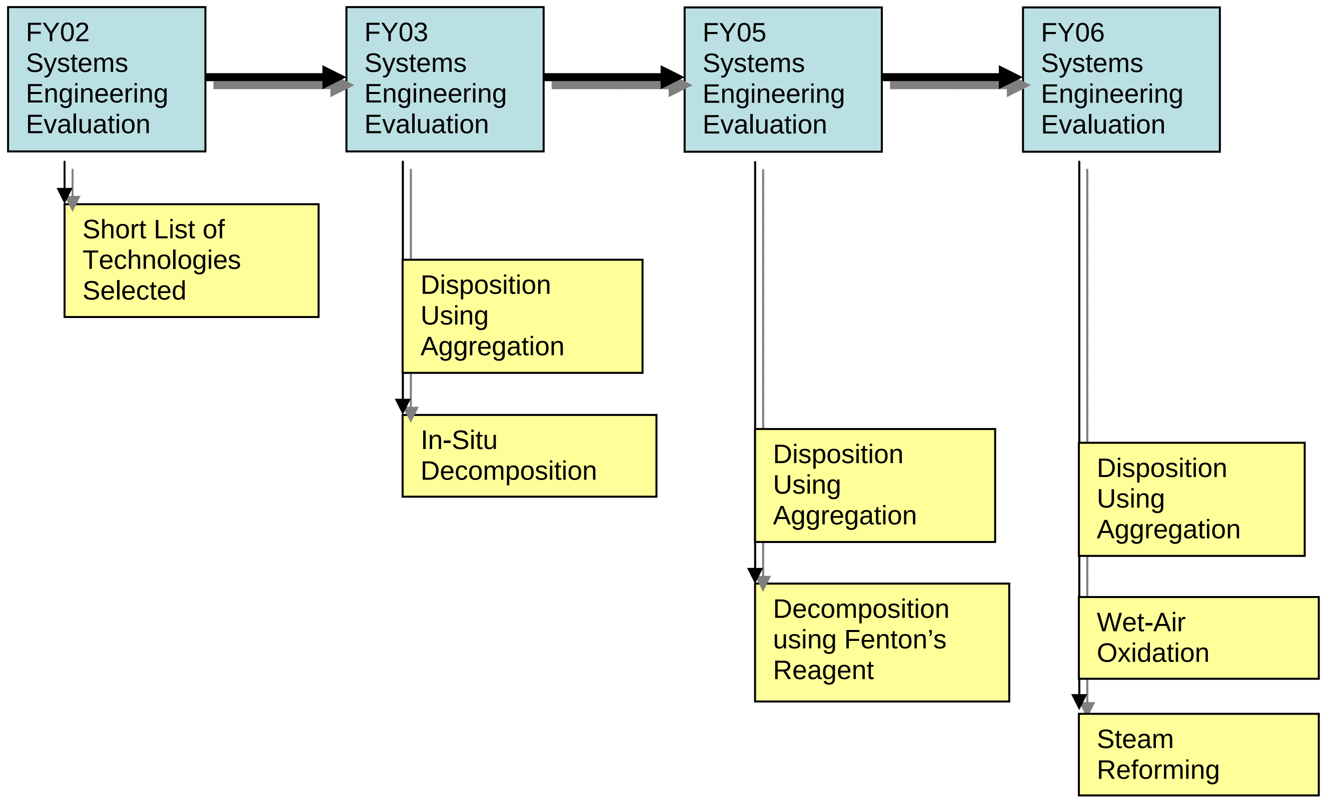


Figure 2. Tank 48 Alternative Evaluation Results

Skill Matrix

Line of Inquiry	Supporting Skill Set
1. Validate completeness of Tank 48 alternatives evaluation: – Have evaluations of Tank 48 disposition actions considered a suitably broad range of alternatives? – Are there attractive alternatives, distinctly different from those already considered, which merit evaluation? – Identify any material differences from either a safe operations or regulatory envelope that could merit a different alternative solution.	1, 2, 6, 12, 14, 17, 19
2. Evaluate the treatment of uncertainty: – Have technical and programmatic uncertainties been adequately taken into account in Tank 48 alternative evaluations?	1, 2, 4, 5, 8, 9, 10, 11, 13, 14, 15, 16, 17, 19, 20
3. Validate the down-selection process: – Are the selection criteria (including screening criteria and weighted evaluation criteria) sound? – Where criteria have changed over the years, have previously rejected candidates been given sufficient re-consideration? – Have the criteria been consistently and fairly applied? – Were the evaluations performed in sufficient rigor to support valid conclusions? – Does the set of alternatives currently remaining (i.e., not rejected from further consideration) support very high confidence in ultimate success?	1, 2, 3, 9, 10, 14, 16, 20
4. Assess the viability of the selected technologies and current path forward: – Is the current path forward (including preferred and backup paths) clearly defined? – Is the current technical and project work adequate (in terms of definition, technical basis, planning, timing, adequacy of resources, etc.) to support waste disposition processing plan (DPP) schedule, process interface and performance needs? – Are cost projections adequately bounded?	1, 3, 9, 10, 12, 16, 17, 18, 20
5. Identify risks and assess adequacy of risk management actions: – Have the technical and programmatic risks associated with the current path forward been thoroughly evaluated? – Are the risk mitigation actions (in place or specifically planned) appropriate for the identified risks? – Are other risk mitigation actions recommended? – Has the impact on downstream facilities been considered? – Has the technical and programmatic risk assessment effectively accounted for the projected safe operations, maintenance, regulatory, process control and environmental risks and their mitigation?	1, 3, 9, 10, 12, 14, 15, 16, 17, 18, 19, 20
6. Identify additional lines of inquiry that should be explored in the evaluation of the viability of the Tank 48 path forward	All skill sets

SKILL SET INVENTORY

1. Chemical Engineering
2. Chemical Process Safety
3. Engineering Management
4. Environmental compatibility
5. Environmental Requirements (DOE, EPA, state, etc.)
6. Familiarity with DOE Complex waste characteristics and history
7. Maintenance requirements
8. Materials compatibility with process conditions and corrosion
9. Mechanical engineering
10. Nuclear Engineering
11. Nuclear materials safety and processing
12. Process engineering
13. Process effluent/process product characterization
14. Process research, development, experimental design
15. Process scale up & design
16. Project Management
17. Waste/radioactive waste treatment technology
18. Waste/radioactive waste operations management
19. Relevant process chemistry
20. Risk Analysis, Assessment, Management

Attachment 3: Proposed ITR Members

Candidate	Credentials	Areas of Expertise / Strengths	Skillset(s) Supported	Primary LOI(s) Supported
1. John (Jack) DeVine, Team Lead	B.S. Mathematics, U.S. Naval Academy. Principal, Polestar Applied Technology; former SRS Chief Closure Officer for WSRC. Former Recovery Engineering Manager and Technical Planning Director for TMI Unit 1; GPU Nuclear Corporation V.P. & Director - Technical Functions; member, Exec. Board, EEI Waste Management Group, GPU Nuclear Board of Directors; directed EPRI ALWR program.	Naval, Commercial, and U.S. DOE nuclear facility operations, engineering, and project management; familiarity with DOE complex waste characterization & history, decontamination and decommissioning.	3, 5, 6, 7, 9, 10, 16, 18, 20	1, 2, 3, 4, 5, 6
2. Edward Cussler, Ph.D.	B.E, M.S., Ph.D., Chemical Engineering. Professor, University of Minnesota. Past President A.I. Ch.E and past chair, American Assoc of Engineering Societies. Member Editorial Board, "Separations," "Journal of Membrane Science," and "A.I.Ch.E. Journal." 150 Journal publications.	Chemistry, separations processes, mass transfer phenomena, radioactive waste treatment technology, familiarity with DOE complex waste characterization & history	1, 2, 6, 8, 11, 13, 14, 17, 19	1, 2, 4, 5, 6
3. Bruce E. Hinkley	B.S.,U.S. Naval Academy, Vice President, Energy Business Unit, InfoZen, Inc.;	Project management, engineering management, Naval, commercial, and U.S. DOE nuclear facility operations, engineering, and project management.	3, 5, 6, 7, 9, 10, 16, 18, 20	3, 4, 5
4. Gary S. Huvard, Ph.D	Associate Professor and Assistant Chair with the Department of Chemical Engineering, Virginia Commonwealth University; B.S., Chemistry, Ph.D, Chemical Engineering	Chemical Engineering, Research and Development. Waste treatment technology.	1, 2, 6, 8, 11, 13, 14, 17, 19	1, 2, 4, 5
5. James A. Kelley, Ph.D	Independent consultant, Retired DuPont Technology Director; B.S., Ph.D., Chemistry; Co-leader for technology sub-team for the WTP External Flowsheet Review	Chemical Engineering, familiarity with DOE Complex waste characterization and history, processing and management.	1, 2, 3, 6, 8, 10, 11, 12, 13, 14, 15, 17, 18, 19	1, 2, 4, 5
6. Eugene J. Kosiancic	B.S. Chemistry, M.S. Nuclear Engineering, Doctoral Studies. Thirty+ years experience in technical support, operations, and management of DOE radioactive waste operations (Hanford). Two patents.	Process engineering, strategic and long-range planning, tank farm operations, chemical processing, systems engineering, risk analysis, familiarity with DOE complex waste characterization & history	1, 2, 3, 4, 5, 6, 7, 8, 10, 11, 12, 13, 16, 17, 18, 19, 20	1, 2, 3, 4, 5, 6

Candidate	Credentials	Areas of Expertise / Strengths	Skillset(s) Supported	Primary LOI(s) Supported
7. David Kosson, Ph.D.	Ph.D., Chemical and Biochemical Engineering. Chair and Professor of Civil and Environmental Engineering, Vanderbilt University.	Chemical Engineering, Waste Treatment Technology, Risk Analysis & Assessment	1, 2, 4, 5, 12, 14, 19, 20	1, 2, 3, 4, 5, 6
8. Anthony L. Pezone	B.S., M.S., Chemical Engineering Independent consultant; retired DuPont Principal Division Consultant.	Chemical Engineering, Process Engineering, Process Development	1, 2, 6, 8, 12, 13, 14, 15, 17	2, 3, 4
9. Lawrence Tavlarides, Ph.D.	B.S., M.S., Ph.D., Chemical Engineering. Professor, Biomedical and Chemical Engineering, Syracuse University. Former department chair and associate Dean. Consultant to commercial industry, National Science Foundation, and DOE. Currently serves as a consultant to the Department of Energy Tank Focus Area for clean up of radioactive nuclear waste. More than 100 archival articles, 38 conference proceedings, 14 patents.	Chemical engineering including thermodynamics, chemical reaction engineering, kinetics, water oxidation, chemical separation technology, mixing, familiarity with DOE complex waste characterization & history; Member, DOE Technology Advisory Team, Consultant, Technical Working Group, Salt Processing Project Technology Selection.	1, 2, 6, 8, 11, 13, 14, 17, 19	1, 2, 3, 4, 5, 6
10. Jack S. Watson, Ph.D.	Ph.D. Chemical Engineering. Consultant, Retired Sr. Research Engineer, ORNL. Past Technical Coordinator for the DOE's Efficient Separations Cross-cutting Technology Program. AIchE Fellow and Author, "Separation for Waste Management," Deker, 2000.	Waste treatment technology, including separation, adsorption, and ion exchange; reprocessing, environmental restorations, familiarity with DOE complex waste characterization & history. 30+ years experience radioactive waste technical support.	1, 2, 6, 8, 11, 13, 14, 17, 19	1, 2, 3, 4, 5, 6
DOE Observer: Joel Case	B.S Microbiology (chemistry minor), M.S. Nuclear Engineering and Environmental Engineering (dual degree). DOE-ID, Federal Project Director, SBW Treatment Project. Led EM-1 independent review evaluating alternative technologies for the SRS In-Tank Precipitation project.	Overall technical and regulatory input; waste treatment technology. Naval, commercial power, and U.S. DOE nuclear facility operations; research and development; familiarity with DOE complex waste characterization & history, project management, risk analysis.	2, 3, 4, 6, 10, 11, 16, 17, 18, 20	2, 3, 4, 5, 6

Attachment 4: ITR Path Forward

The following path forward outlines the anticipated sequence and duration of ITR activities and is presented to serve as a planning basis. For activities subsequent to the kick-off meeting, ongoing ITR work may dictate changes to the duration and dates shown.

	Week	Tank 48 Independent Technical Review
5/8 – 5/12		WSRC Finalize and submit to DOE-SR complete TANK 48 ITR planning package, including process, charters, proposed membership and tentative schedule
5/15 – 5/19		– DOE-SR review, approve and submit the planning package to DOE-HQ for review and approval – DOE-HQ concur with charter and personnel selection
5/22 – 5/26		– WSRC let contracts for approved team members – WSRC submit proposed review package, for DOE-HQ approval
5/29 – 6/2 (Memorial Day week)		– WSRC distribute review packages to team members – Conference call with team to resolve any outstanding questions – Finalize and issue agenda for kickoff meeting – Release members to travel
6/5 – 6/8	1	**Review Team on site (T-F)** – **Kickoff Meeting** – Technical briefings and tours – Agreement on scope, level of detail, sub-assignments and rough outline of report – Identification of any additional specialty skills required
6/12 – 6/16	2	– Independent review – Conference call meeting
6/19 – 6/23	3	**Team on site (M-F)** – Continued reviews, discussions, interviews – Establish findings re completeness and validity of prior TANK 48 assessments – Mid-point review with WSRC and DOE management
6/26 – 6/30	4	– Independent review – Conference call meeting
7/3 – 7/7 (July 4th week)	5	– Independent review – Conference call meeting
7/10 – 7/14	6	**Team on site (T-F)** – Final discussions with staff, team interactions and determination of findings and recommendations
7/17 – 7/21	7	– Submit report draft material, as assigned
7/24 – 7/28	8	– Issue draft report for team review
7/31 – 8/3	9	– Team comments on draft – Conference call meeting(s) to resolve open comments – Incorporate all comment resolutions and prepare final report
8/7 – 8/10	10	**Approve & Issue Final Report**
8/14 – 8/18	11	– Out-brief to WSRC and DOE management; team participation on-site as desired

APPENDIX 2: ITR TEAM CREDENTIALS

Candidate	Credentials	Areas of Expertise / Strengths
1. John (Jack) DeVine, Team Lead	B.S. Mathematics, U.S. Naval Academy. Principal, Polestar Applied Technology; former SRS Chief Closure Officer for WSRC. Former Recovery Engineering Manager and Technical Planning Director for TMI Unit 1; GPU Nuclear Corporation V.P. & Director - Technical Functions; member, Exec. Board, EEI Waste Management Group, GPU Nuclear Board of Directors; directed EPRI ALWR program.	Naval, Commercial, and U.S. DOE nuclear facility operations, engineering, and project management; familiarity with DOE complex waste characterization & history, decontamination and decommissioning.
2. Thomas M. Crimmins	B.S. Physics, College of the Holy Cross, M.S. Engineering Management, New Jersey Institute of Technology; Consultant, Polestar Applied Technology, Inc.; former President and Chief Executive Officer, BNFL, Inc. (now British Nuclear- America); former Vice President-Nuclear Engineering, Public Service Electric and Gas Company; former Site Manager, Susquehanna Nuclear Generating Station, Pennsylvania Power and Light Company; formerly Director, American Nuclear Society; Member, Board of Directors, numerous companies; Member, numerous Nuclear Power Plant Independent Safety Review Committees.	Commercial, nuclear and USDOE nuclear facility operations, engineering, safety analyses and project management; waste management, decontamination and decommissioning, communication of technical issues and technical strategy development and planning.
3. Edward Cussler, Ph.D.	B.E, M.S., Ph.D., Chemical Engineering. Professor, University of Minnesota. Past President A.I. Ch.E and past chair, American Assoc of Engineering Societies. Member Editorial Board, “Separations,” “Journal of Membrane Science,” and “A.I.Ch.E. Journal.” 150 Journal publications.	Chemistry, separations processes, mass transfer phenomena, radioactive waste treatment technology, familiarity with DOE complex waste characterization & history

Candidate	Credentials	Areas of Expertise / Strengths
4. Bruce E. Hinkley	B.S.,U.S. Naval Academy, Vice President, Energy Business Unit, InfoZen, Inc.;	Project management, engineering management, Naval, commercial, and U.S. DOE nuclear facility operations, engineering, and project management.
5. Gary S. Huvard, Ph.D	Associate Professor and Assistant Chair with the Department of Chemical Engineering, Virginia Commonwealth University; B.S., Chemistry, Ph.D, Chemical Engineering	Chemical Engineering, Research and Development. Waste treatment technology.
6. James A. Kelley, Ph.D	Independent consultant, Retired DuPont Technology Director; B.S., Ph.D., Chemistry; Co-leader for technology sub-team for the WTP External Flowsheet Review	Chemical Engineering, familiarity with DOE Complex waste characterization and history, processing and management.
7. Eugene J. Kosiancic	B.S. Chemistry, M.S. Nuclear Engineering, Doctoral Studies. Thirty+ years experience in technical support, operations, and management of DOE radioactive waste operations (Hanford). Two patents.	Process engineering, strategic and long-range planning, tank farm operations, chemical processing, systems engineering, risk analysis, familiarity with DOE complex waste characterization & history
8. David Kosson, Ph.D.	Ph.D., Chemical and Biochemical Engineering. Chair and Professor of Civil and Environmental Engineering, Vanderbilt University.	Chemical Engineering, Waste Treatment Technology, Risk Analysis & Assessment
9. Anthony L. Pezone	B.S., M.S., Chemical Engineering Independent consultant; retired DuPont Principal Division Consultant.	Chemical Engineering, Process Engineering, Process Development
10. Lawrence Tavlarides, Ph.D.	B.S., M.S., Ph.D., Chemical Engineering. Professor, Biomedical and Chemical Engineering, Syracuse University. Former department chair and associate Dean. Consultant to commercial industry, National Science Foundation, and DOE. Currently serves as a consultant to the Department of Energy Tank Focus Area for clean up of radioactive nuclear waste. More than 100 archival articles, 38 conference proceedings, 14 patents.	Chemical engineering including thermodynamics, chemical reaction engineering, kinetics, water oxidation, chemical separation technology, mixing, familiarity with DOE complex waste characterization & history; Member, DOE Technology Advisory Team, Consultant, Technical Working Group, Salt Processing Project Technology Selection.

Candidate	**Credentials**	**Areas of Expertise / Strengths**
11. Jack S. Watson, Ph.D.	Ph.D. Chemical Engineering. Consultant, Retired Sr. Research Engineer, ORNL. Past Technical Coordinator for the DOE's Efficient Separations Cross-cutting Technology Program. AIchE Fellow and Author, "Separation for Waste Management," Deker, 2000.	Waste treatment technology, including separation, adsorption, and ion exchange; reprocessing, environmental restorations, familiarity with DOE complex waste characterization & history. 30+ years experience radioactive waste technical support.
DOE Observer: Joel Case	B.S Microbiology (chemistry minor), M.S. Nuclear Engineering and Environmental Engineering (dual degree). DOE-ID, Federal Project Director, SBW Treatment Project. Led EM-1 independent review evaluating alternative technologies for the SRS In-Tank Precipitation project.	Overall technical and regulatory input; waste treatment technology. Naval, commercial power, and U.S. DOE nuclear facility operations; research and development; familiarity with DOE complex waste characterization & history, project management, risk analysis.

APPENDIX 3: ITR Review of Tank 48 Alternatives

Bins: **A: Attractive candidate**
B: Potentially attractive
C: Unattractive

Candidate	ITR Bin	Sched	Cost	Success Confidence	Regulatory & Permitting	SRS Process Compatibility	Physical Practicality	Real Safety	Other Comment
Acid hydrolysis In tank	C			Pitting – corrosion concerns at Low pH (Passivating may be possible, but impractical)					
Acid hydrolysis In small reactor in tank riser	C				uncertain		Difficult working environment		
Acid hydrolysis In Canyon	C		High		Canyon not permitted	Processing window	Canyon not available		
Acid hydrolysis In DWPF salt cell	C		Very high				Cell no longer available		Tars
Acid hydrolysis In new unit (241-96H)	A	Schedule compara ble to other 241-96H options (4-6y)	Cost comparable to other 241-96H options	▪ Technology works ▪ Process Rate uncertain – need more data	Benzene management		Need to find or create the new space	Benzene management	External Chemical Process – <u>decomposition</u> of TPB (cook option)
Fenton's In Tank	C			Pitting – pH decreases over time				Peroxide handling	
Fenton's in 241-96H	B	Schedule compara ble to other 241-96H	Cost comparable to other 241-96H options	▪ Low temp "burn" option ▪ Uncertainty in rates	Potentially less benzene management problem (relative to "cooking"			Peroxide handling	External Chemical Process – <u>destruction</u> of TPB (burn

Candidate	ITR Bin	Sched	Cost	Success Confidence	Regulatory & Permitting	SRS Process Compatibility	Physical Practicality	Real Safety	Other Comment
		options (4-6y)			options)				option)
Oxidation by Permanganate (all versions)	C		Lifecycle cost			Excessive glass production (DWPF)			Unattractive because of glass implications
Filter in ARP, then decompose in Tank 48	C			Doesn't solve the problem, creates new ones					Possible enhancement
Photolytic decomposition	C			Opaque solution					tough
Decant (or otherwise concentrate and separate)	C			Doesn't solve the problem – residual solids are still a problem					Could be part of a decoupling option, with reduced volume requirement
Solubilize TPB, then run Tank 49 chemistry	B			▪ Strong concept, needs testing and data ▪ T49 experience is valuable	Benzene management	Requires adding organics to Tank 48			Uncertain, but very high potential – elegant solution (if it works)
Decomposition, in and out of tank	C			Does not work (too slow)					
Steam Reforming, in 241-96H	A	3-5 years	High, but in line with other processing options	▪ Technical prospects are good ▪ Consider higher capacity unit ▪ Demonstrated on rad applications and piloted with Tank 48	No major barriers	No issues	Tight fit in 241-96H	manageable	Product is a soluble solid

Candidate	ITR Bin	Sched	Cost	Success Confidence	Regulatory & Permitting	SRS Process Compatibility	Physical Practicality	Real Safety	Other Comment
				simulant					
Wet air oxidation	A	4-6 years	High, but in line with other processing options (high pressure could drive cost up)	▪ Appears attractive, but based on limited data on similar materials ▪ Significant adaptation req'd for rad service	No major barriers	No issues		High pressure (~100atm)	Product is aqueous solution
DWPF Melter - all options	C					Negative implications wrt DWPF compatibility		Flammability	
DWPF – slow bleed into sludge batch (pure dilution)	C	30 years							12KG of KTPB in a one million gallon batch; possibly useful in combination with other actions
CIF (Incinerator)	C			Contact handled incinerator – poor application for this waste	Was licensed for LLW				
Evaporator	C			Uncertain effectiveness		Could interfere with evaporator needs and/or compromise evaporator performance	▪ Requires mods to contaminated equipment ▪ 2H feed tank (43) would become contaminated with TPB and tars		

Candidate	ITR Bin	Sched	Cost	Success Confidence	Regulatory & Permitting	SRS Process Compatibility	Physical Practicality	Real Safety	Other Comment
Aggregation	A	Good (except for permit time frame)	Least cost	▪ Simple process, low technical risk ▪ Analysis of aggregate benzene release is important	Hi risk – SC concern re curies left on site	▪ Potential impact on Saltstone operation ▪ Simultaneous need to deal with MCU isopar		No issue	Strong potential as a partial solution (part of combined approach)

APPENDIX 4: STEAM REFORMER CALCULATIONS

Calculations on Steam Reforming geometry were made for the two scenarios assuming one year of processing at 50% up time.

Case 1: 74 Kgal supernate as a concentrate with 10wt% solids at six months processing time

Case 2: 250 Kgal supernate with 3wt% solids processed in the Steam Reforming geometry required for Case 1

The reducing bed and the oxidizing bed volumes and geometries were estimated at operating conditions similar to those in the STAR pilot study. The size of the reducing bed was estimated by maintaining geometric similarity between the commercial scale unit and the pilot scale unit and using the ratio of commercial/pilot solids flow rates to scale the volume. The residence times could not be calculated as dissolved solids were not known in the pilot study. The residence time of solids in the reducing bed was estimated to be between 10 to 20-hours. The scale up procedure used necessarily maintains the residence time of solids in the bed, whatever the value in the pilot study actually was. The lower solid residence times are expected to be effective based on the crucible studies.

The reaction times to destroy benzene and to form solids from the feed are of the order of 10 seconds or less. The oxidizer reactor volumes were estimated assuming a first order benzene destruction rate. The pilot study benzene conversion of 94% at a vapor phase residence time of 6.6 seconds was used to estimate a rate coefficient. Instantaneous destruction of KTPB to benzene was assumed because of the >99.98% (within detection limits) destruction of KTPB to benzene in the proof of principle pilot studies, similar results in all the crucible studies (no 3PB, 2PB, PB), and KTPD decomposition study results at 400°C reported by Fondeur [WSRC-TR-99-00023]. The rapidity of the decomposition at 400°C has also been confirmed experimentally Huvard [Private Communication, *Thermogravimetric Analysis of KTPB Powders Showed Quantitatively Complete Loss of Benzene from KTPB after 5-10 Minutes at 400°C.*]. The steam and atomization gas rates were proportional to those used in the pilot study.

Calculation conditions are in Table A4-1 and reducing bed geometry results are in Table A4-2. The reducing bed geometries for Case 1 and Case 2 are the same as those computed for Case 1 Steam Reforming conditions. An acceptable size of ~ 17-inches diameter with ~ 8.3-feet height was estimated. Approximately 5 additional feet would be required for the cyclone and free board space. Six months processing time is estimated to process the concentrated 74 Kgal supernate (10wt% solids). This Steam Reforming would require ~17 months to process the 250 Kgal supernate (3wt% solids) at the same solids residence time

In Table A4-3, the estimated volumes are recorded for an oxidizer reactor as configured at STAR for 94%, 99%, and 99.9% conversions of benzene by assuming that all benzene split from the KTPB was released from the reducing bed and oxidized in the upper section of the STAR reactor. The pilot study benzene conversion of 94% for a vapor phase residence time of 6.6 seconds was used to estimate a first order rate coefficient needed to carry out the volume estimates. Although these calculations have been carried out, the Team is not at all sure that benzene was actually oxidized in the upper section of the STAR reactor as the pilot reactor temperature was relatively low (650°C versus 800-900°C), there was no catalyst in the oxidizing section of the reactor, and the oxygen flow rate to the unit was well below the stoichiometric requirement for oxidizing benzene. Instead, the Team believes that most of the benzene reacted with water vapor in the reducing bed to form CO and H_2. Hydrogen formed in the reducing section would have competed very effectively for available oxygen with any unreacted benzene in the upper section of the reactor. Thus, obtaining high benzene destruction rates (99.9%+) may require the use of a second catalytic fluidized bed run under oxidizing conditions in lieu of a gas phase reactor above the reducing bed as employed in the STAR study, a configuration also suggested by researchers at Hazen Research, Inc.

Thus, a steam reformer sized to process a concentrated Tank 48 waste stream (10wt% solids) in six months can fit in the 241-96H facility. The same steam reformer would require ~17 months to process the 250 Kgal supernate (3wt% solids). A STAR-type gas phase oxidizer reactor sized for 99% benzene conversion may fit in 241-96H as well, but a second fluidized bed run as an oxidizer will be more effective and more compact than the vapor phase oxidation zone used in the STAR reactor configuration. A commercial catalytic oxidizer may be considered as an alternative to an oxidizing fluid bed reactor.

Cases		1 74,200gal, 10wt% solids	2 250,000gal, 3wt% solids
1	Supernate (gal)	67,500	243,300
2	V solid (gal)	6,700	6,700
	Total Vol (gal)	74,200	250,000
3	Mass Supernate (Kg)	297,540	1,072,500
4	Mass H_2O/Supernate (Kg)	953,300	264,440
5	Mass Dissolved Solids (Kg)	33,100	119,200
6	Mass KTPB Solids (Kg)	19,976	19,976
7	Mass Other Solids (Kg)	13,084	13,084
8	Total Mass (Kg, 3+6+7)	330,640	1,105,600
9	Mass as Benzene (Kg)	17,394	17,394
10	Solids To Bed (Kg, 5+6+7)	66,162	152,262
11	Solids Remaining in the Bed (Kg, 10-9)	48,768	134,868
	Temperature, °C	650	650
Processing Rate (50%,1yr)[a]			
Vol Flow Rates			
12	Water (m3/min)	14.0	18.4
13	Atomizing Gas (m3/min)	2.4	3.2
14	Benzene (m3/min)	0.064	0.017
15	Total (m3/min)	16.4	21.6
16	$[\text{Benzene}]_o$ (kmol/min)$\times 10^5$	5.2	1.4
17	Total Solids Processing Rate (Kg/min)	0.25	0.25
18	Total Supernate/Solids Processing Rate (GPM)	0.30	0.39

Steam Rate (mass) = 2 × Supernate rate, Atomizing Gas = 1.16 × Supernate rate

Table A4-1: Conditions for Tank 48H Case Studies

Cases	Proc Vol Kgal	wt% Solids	T °C	P atm	X KTPB mol frac	Proc time (mos)	τ_{solids} hr	V m^3	D_{FB} ft	H_{FB} ft
1	74	10	650	1	0.9998	6	10-20	0.3	1.4	6.8
2	250	3	650	1	0.9998	17	10-20	0.3	1.4	6.8

[a] The residence time depends on the bulk density of the solids and the bed expansion during fluidization.

Table A4-2: Steam Reforming Calculated Geometry for Reducing Bed for Dissolved and Insoluble Solids Processing

Cases	Proc Vol Kgal	wt% Solids [-]	Vapor[a] Rate m^3/min	T °C	P atm	X Fractional Conversion	τ_{gas} s	V m^3	D_{FB} ft	H_{FB} ft
1	74	10	16.2	650	1	0.94	6.6	1.8	2.5	13
	74	10	16.2	650	1	0.99	32	8.9	4.2	22
	74	10	16.2	650	1	0.999	49	13	–	–

[a] Vapor consists of water from the supernates, the fluidizing steam, and the atomizing gas.

Table A4-3: Steam Reforming Calculated Geometry for Oxidizing Bed for Benzene Destruction

APPENDIX 5: TANK 48 CONCENTRATIONS

Tank 48H Radiological and Chemical Compositions

Tank 48H contains approximately 250 Kgal of a radioactive alkaline slurry (pH 14) with roughly 2.3wt% solids (<10 μm). The solids consist of a mixture of MST, TPB salts, and entrained metal hydroxide sludge. The potassium and KTPB and CsTPB) salts resulted from precipitation after addition of sodium NaTPB.

	Slurry (dpm/ml)	Supernate (dpm/ml)
Cs-137	1.01E+09	3.0E+07
Gross Alpha	3.44E+06	NM
Sr-90	7.34E+05	NM
	(Mg/L)	**(Mg/L)**
Tc-99	2.26E+00**	2.26E+00
Th-232	NM	1.95E-02
Np-237	2.83E-01	5.39E-02
Pu-239	4.46E-02	2.80E-03
Pu-238	8.82E-02	1.77E-02
Pu-240*	5.67E-03*	NM
Pu-241*	9.36E-04*	NM
U-233	9.44E-02	4.94E-02
U-234	4.99E-01	3.58E-01
U-235	9.71E-01	5.74E-01
U-236	1.48E+00	1.41E+00
U-238	6.16E+00	3.62E+00
U Total	6.32E+00	6.01E+00
Total Pu	1.36E-01	2.05E-02

*The current Tank 48 waste volume is approximately 238,000 gallons (this value is for solids only) [CBU-PIT-2005-00046].

Table A5-1: Tank 48 Radiological Characterization Summary

Tank 48 Chemical Characterization

A Tank 48 chemical characterization has been developed to support material disposition. In this characterization, values are based on the most conservative of three recent samples results (Sep-03, Aug-04, and Mar-05). The exceptions are the concentration of TPB and KTPB, which are based on a statistical analysis of sample data. Previous calculations show that the amount of KTPB in the tank is in the range of 19,000 Kg to 26,400 Kg. The statistical analysis indicates that the upper 95% confidence limit of the KTPB inventory is 21,800 Kg, which is within this range. Tank 48 Chemical (also called Non-Radiological) Characterization summary is shown in Table A5-2 [CBU-PIT-2005-00066].

CONSTITUENT	CONCENTRATION ESTIMATE			TANK TOTAL	
	Slurry (Mg/L)	Supernate (Mg/L)	Calc Dry Solids (Mg/L)	(Kg)	
TPB	2.12E+04	<10	2.12E+04	1.94E+04	Refer to Section 4.1
Calculated KTPB	2.38E+04	NM	NM	2.18E+04	
Phenol	9.73E+02	7.06E+02	2.67E+02	8.91E+02	
BiPhenyl	6.32E+02	<10	6.32E+02	5.79E+02	
Triphenylborate (3PB)	1.62E+02	<10	1.62E+02	1.48E+02	
Biphenylborate (2PB)	1.42E+02	<10	1.42E+02	1.30E+02	
Phenylborate (1PB)	1.51E+02	<10	1.51E+02	1.38E+02	
Nitrobenzene	<50	<10	NM	<4.58E+01	
Nitrosobenzene	<50	<10	NM	<4.58E+01	
o-terphenyl	<50	<10	NM	<4.58E+01	
m-terphenyl	<50	<10	NM	<4.58E+01	
p-terphenyl	<50	<10	NM	<4.58E+01	
benzene	5.6E+01	<10	5.6E+01	5.13E+01	
Ag	1.88E-02	2.12E-03	1.67E-02	1.72E-02	Refer to Section 4.2
Pd	9.28E-02	7.37E-02	1.91E-02	8.50E-02	
Cu	4.0E+00	1.01E+00	2.99E+00	3.66E+00	
Cd	2.16E-02	1.57E-02	5.90E-03	1.98E-02	
Hg	2.20E+01	6.73E-02	2.19E+01	2.02E+01	
Rh	2.30E-01	1.09E-01	1.21E-01	2.11E-01	
Ru	3.80E-01	2.93E-01	8.70E-02	3.48E-01	
B	1.03E+03	4.60E+02	5.70E+02	9.43E+02	Refer to Section 4.3
Fe	1.69E+02	<2.14E-01	1.69E+02	1.55E+02	
K	2.65E+03	2.55E+02	2.40E+03	2.43E+03	
Na	8.80E+04	8.80E+04	~0	8.06E+04	
Al	2.31E+03	2.31E+03	~0	2.12E+03	
Ca	4.30E+01	6.42E-01	4.24E+01	3.94E+01	
Cr	7.0E+01	4.75E+01	2.25E+01	6.41E+01	
Mn	7.82E+00	3.60E-02	7.78E+00	7.16E+00	
Mg	2.02E+01	<0.058	2.02E+01	1.85E+01	
Ba	3.47E+00	<0.117	3.47E+00	3.18E+00	

Table A5-2: Tank 48 Chemical Characterization Summary

Tank 48 Chemical Characterization Summary (Continued)

CONSTITUENT	CONCENTRATION ESTIMATE			TANK TOTAL	
	Slurry (Mg/L)	Supernate (Mg/L)	Calc Dry Solids (Mg/L)		
As	<4.6	NM	NM	<4.21E+00	Refer to Section 4.3
Pb	<2.83E-01	<2.83E-01	NM	<2.59E-01	
Se	<4.8	NM	NM	<4.40E+00	
Co	NM	NM	NM	NM	
Li	9.9E-01	9.9E-01	NM	9.07E-01	
Mo	1.33E+01	9.94E+00	3.36E+00	1.22E+01	
Ni	<1.5E-02	<1.5E-02	NM	<1.37E-02	
P	2.41E+02	2.41E+02	~0	2.21E+02	
S	3.78E+02	3.2E+02	5.8E+01	3.46E+02	
Sb	1.15E+01	6.87E+00	4.63E+00	1.05E+01	
Si	1.25E+02	6.67E+00	1.18E+02	1.15E+02	
Sn	2.21E+01	4.92E+00	1.72E+01	2.02E+01	
Sr	9E+00	<3.12E-01	9E+00	8.24E+00	
Ti	8.40E+02	<1	8.40E+02	7.69E+02	
U	5.31E+00	1.1E+00	4.21E+00	4.86E+00	
V	8.89E-01	8.89E-01	~0	8.14E-01	
Zn	1.19E+01	5.41E+00	6.63E+00	1.09E+01	
Zr	1.47E+00	1.47E+00	NM	1.35E+00	
Gd	<0.01	<0.01	NM	<9.16E-03	
La	<0.032	<0.032	NM	<2.93E-02	
Total Organic Carbon	2.14E+04	3.01E+03	1.84E+04	1.96E+04	
Br^-		<91		<8.34E+01	Refer to Section 4.4
F-		1.4E+01		1.28E+01	
Cl-		3.70E+02		3.39E+02	
CO_2H-		6.80E+02		6.23E+02	
$C_2O_4^{2-}$		1.61E+03		1.48E+03	
NO_2^-		2.14E+04		1.96E+04	
NO_3^-		1.34E+04		1.23E+04	
PO_4^{3-}		9.16E+02		8.39E+02	
SO_4^{2}-		5.28E+02		4.84E+02	
NH_4^+		NM		NM	
CO_3^{2-}		4.92E-01 M		2.70E+04	
OH^-		1.34E+00 M		2.09E+04	
Total Base		2.49E+00 M		n/a	
Other Base (excluding CO_3^{2-})		2.67E-01 M		n/a	
Density, g/mL	1.165 g/mL	1.164 g/mL	n/a	n/a	Refer to Section 4.5
Total Solids, wt%	20.19wt%	17.68wt%	n/a	n/a	
MST solids, wt%	0.15 wt%	<0.0024wt%	n/a	n/a	
Total Insolubles, wt. %	3.05wt%	NM	n/a	n/a	
KTPB wt%	2.01wt%	<0.001wt%	n/a	n/a	

APPENDIX 6: ESTIMATING Cs-137 AND TPB IN FILTRATE

To begin the chemical treatment of Tank 48 contents, the Team considered filtration producing a 10wt% slurry as a reaction feed. This step also produces a filtrate containing Cs-137 and TPB. The Team estimates the amount of Cs-137 and TPB in this stream and the amount of benzene potentially evolved through TPB degradation. Appendix 4, Table A4-1, and Appendix 5, Table A5-1 are the source of the numbers used in the following calculations.

As shown in Appendix 5, the concentration of Cs-137 in the tank slurry is about 1.01×10^9 dpm/ml with the supernate at 3.0×10^7 dpm/ml. By filtration, about two thirds of the soluble Cs-137 is removed and send it to Saltstone. This results in approximately 2% of the Cs-137 processed into Saltstone.

$$\frac{2}{3} \times 3.0 \times 10^7 \, \frac{dpm}{ml} \times 1.01 \times 10^9 \, \frac{1ml}{dpm} \times 100 = 2\%$$ [15]

To estimate the amount of benzene that may be potentially evolved, the Team assumed 250 Kgal (11.5×10^5 Kg) total in Tank 48. This contains about 20,000 Kg KTPB. The weight of filtrate is 7.7×10^5 Kg.

The concentration of TPB in the filtrate is too small to measure, as shown in reference PIT-MISC-0176. To estimate this concentration, the Team recognizes that the solubility of $K[B(C_6H_5)_4]$ is 1.8×10^{-4}M. The solubility product, K_{sp} can then be defined.

$$K_{sp} = [K^+]\,[B(C_6H_5)_4]$$

$$= [1.8 \times 10^{-4}]\,[1.8 \times 10^{-4}] = 3.2 \times 10^{-8} M^2$$

(Note, this does not consider the actual activity coefficients in response to a high ionic strength solution but is a reasonable first approximation.)

But in the actual filtrate, the potassium concentration is 248×10^{-3} g/l, or 6.4×10^{-3} mol/l. Thus

$$3.2 \times 10^{-8}\, M^2 = [6.4 \times 10^{-3}]\,[B(C_6H_5)_4]$$

$$[B(C_6H_5)^-_4] = 5.0 \times 10^{-6}\, M$$

[15] Values used for some calculations are made using approximate values based on input from multiple sources. These approximations do not effect the conclusions or recommendation of the report.

This is equivalent to 1.8 Mg/l if the TPB is completely degraded to benzene, much less than the 10 Mg/l which can be measured.

From Table A4-1, the mass of filtrate is:

1,072,500 - 297,540 = 774,960 or 7.7x 10^5

Therefore:

$$7.7 \times 10^5\ Kg \times \frac{1\,Liter}{1.16\,Kg} \times \frac{1.8\,mg}{Liter} \times \frac{1\,Kg}{1 \times 10^6\ mg} = 1.195 Kg$$

The total amount of benzene that may potentially be evolved during TPB degradation is 1.2 Kg.

This is in addition to the estimated 877 Kg phenol and 570 Kg biphenyl initially present in the Tank 48 supernate. This estimate approximates the solution as ideal.